
EXHIBIT A

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Kaneshiro et al.

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(54) **POLYIMIDE FILM FOR FLEXIBLE
PRINTED BOARD AND FLEXIBLE PRINTED
BOARD USING THE SAME**

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See application file for complete search history.

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(57) **ABSTRACT**

The present invention provides a flexible printed circuit
which is free from curl, torsion and warpage due to tem-
perature change and excellent flexural endurance. By using
polyimide film having an average coefficient of thermal
expansion of 1.0×10^{-5} to 2.5×10^{-5} cm/cm/° C. in a tempera-
ture range of 100° C. to 200° C. and a stiffness value of 0.4
to 1.2 g/cm as the base film for the flexible printed circuit,
a flexible printed circuit having excellent thermal dimen-
sional stability and flexural endurance can be prepared.

5 Claims, No Drawings

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**POLYIMIDE FILM FOR FLEXIBLE
PRINTED BOARD AND FLEXIBLE PRINTED
BOARD USING THE SAME**

RELATED APPLICATIONS

This application is a nationalization of PCT Application No. PCT/JP02/10117 filed Sep. 27, 2002. This application claims priority from Japanese Patent Application No. 2001-303219 filed on Sep. 28, 2001.

1. Technical Field

The present invention relates to a flexible printed circuit which is free from curl, torsion and warpage due to temperature change and also has excellent flexural endurance, and a base film thereof.

2. Background Art

Previously a flexible printed circuit (hereinafter referred to as FPC) has mainly been used in narrow spaces within a camera in a folded form, utilizing its flexibility. Recently, however, flexible printed circuits have come to be used in drive units of floppy disc drives, hard disc drives, copy machines and printers and therefore enhancement of the flexural endurance of flexible printed circuits is required. To enhance the flexibility of the base film, a film made from polyimide having a chemical structure providing high bending property can be used. However, polyimide having high bending property generally has a high coefficient of thermal expansion (CTE), so a flexible printed circuit using the polyimide film as an insulating material has the disadvantage that warpage and curl easily occur. By contrast, when polyimide having a low coefficient of thermal expansion is selected, problems occur such as the film loses flexibility and becomes fragile and the bending property of the obtained FPC decreases.

In light of the above situation, the present invention aims to provide a flexible printed circuit which has excellent thermal dimensional stability and flexural endurance regardless of chemical structure and is free from curl, torsion and warpage due to temperature change without losing ease in handling the base film, and a base film thereof.

DISCLOSURE OF INVENTION

The present invention relates to a polyimide film for a flexible printed circuit, wherein the average coefficient of thermal expansion in the temperature range of 100° C. to 200° C. is 1.0×10^{-5} to 2.5×10^{-5} cm/cm/° C. and the stiffness value is 0.4 to 1.2 g/cm.

The present invention also relates to the above-mentioned polyimide film for a flexible printed circuit comprising polyimide obtained from diamine containing 4,4'-oxydianiline and paraphenylenediamine in a mole ratio of 9/1 to 4/6.

The present invention also relates to a flexible printed circuit comprising an adhesive layer and/or a conductor layer and an insulation material, characterized in that the insulation material is the above-mentioned polyimide film.

Furthermore, the present invention relates to a flexible printed circuit, wherein the number of flexes is at least 10 million times

**BEST MODE FOR CARRYING OUT THE
INVENTION**

The polyimide film for a flexible printed circuit and a flexible printed circuit using the same of the present invention are described below based on one example of the embodiments.

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It is important for the polyimide film of the present invention to adjust the stiffness value to 0.4 to 1.2. The inventors of the present invention found that the flexural endurance of a film is related to the stiffness value and when the value is 0.4 to 1.2, the film has excellent flexural endurance.

The stiffness value is determined by $k \times (\text{film thickness})^3 \times$ (elastic modulus of the film) (k is a proportional constant). These values can be determined so that the stiffness value becomes 0.4 to 1.2, but the film thickness is preferably 17 to 25 μm , more preferably 17 to 23 μm and most preferably 18 to 22 μm . In the case that the film thickness is above the range, the flexural endurance is likely to decrease. In the case that the thickness is below the range, ease in handling the film is likely to decrease.

In the present invention, the film thickness is defined as follows.

In the cases of both a long sheet film and a sheet type film, the film is randomly cut out into the size of a sample for a flexural endurance experiment (180×25 mm) defined by JPCA-FC01 and the thickness is the average of ten points measured in equal intervals in the longitudinal direction from the central area by a contact thickness meter.

When the film thickness fulfills the following equation (1), preferable results regarding flexural endurance can be obtained.

$$X_{\max} - X_{\min} = aX_{\text{ave}} \quad (1)$$

X_{\max} : the maximum value of the 10 points

X_{\min} : the minimum value of the 10 points

X_{ave} : the average value of the 10 points

In the equation, 'a' is at most 0.3, preferably at most 0.2 and further preferably at most 0.1.

Furthermore, the elastic modulus of the film is preferably 350 to 600 kg/mm², more preferably 380 to 550 kg/mm², further preferably 400 to 500 kg/mm², most preferably 400 to 450 kg/mm². In the case that the elastic modulus is below the range, warpage tends to develop in the FPC. In the case that the elastic modulus is above the range, the average coefficient of thermal expansion in the temperature range of 100° to 200° C. can be out of the preferable range.

The polyimide film for a flexible printed circuit of the present invention, for example, can be prepared by flow casting an organic solvent solution of polyamide acid, which is a precursor of polyimide, onto a supporting body such as an endless belt or stainless drum, then drying and imidizing.

As a process of preparing the polyamide acid used in the present invention, known processes can be used. Polyamide acid is usually produced by a process comprising dissolving substantially equimolar amounts of at least one kind of aromatic tetracarboxylic dianhydride and at least one kind of diamine in an organic solvent, and then stirring the obtained polyamide acid organic solvent solution under a controlled temperature until polymerization of the above-mentioned acid dianhydride and the diamine is completed. This polyamide acid solution is obtained usually in a concentration of 5 to 35% by weight, preferably 10 to 30% by weight. When the concentration is within the range, a suitable molecular weight and solution viscosity can be obtained.

As the process for polymerization, any known process can be used and the following are examples of particularly preferable processes for polymerization. That is, there are processes such as:

1) A process comprising dissolving aromatic diamine in an organic polar solvent and then polymerizing by reacting

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- the solution with a substantially equimolar amount of aromatic tetracarboxylic dianhydride,
- 2) A process comprising reacting an aromatic tetracarboxylic dianhydride and an aromatic diamine compound of a much smaller molar amount compared to the dianhydride in organic polar solvent, producing a pre-polymer having an acid anhydride group at both ends and then polymerizing by using an aromatic diamine compound so that substantially equimolar amounts of the aromatic tetracarboxylic dianhydride and the aromatic diamine compound are used in total,
 - 3) A process comprising reacting an aromatic tetracarboxylic dianhydride and an aromatic diamine compound of a much larger molar amount compared to the dianhydride in an organic polar solvent, producing a pre-polymer having an amino group at both ends and then after additionally adding an aromatic diamine compound, polymerizing by using an aromatic tetracarboxylic dianhydride so that substantially equimolar amounts of the aromatic tetracarboxylic dianhydride and the aromatic diamine compound are used in total,
 - 4) A process comprising dissolving and/or dispersing an aromatic tetracarboxylic dianhydride in an organic polar solvent and then polymerizing by adding an aromatic diamine compound so that substantially equimolar amounts of aromatic tetracarboxylic dianhydride and the aromatic diamine compound are used in total,
 - 5) A process of polymerizing by reacting a mixture containing substantially equimolar amounts of an aromatic tetracarboxylic dianhydride and an aromatic diamine in an organic polar solvent.

These processes can be selected suitably according to the desired properties.

Below, the materials used for the polyamide acid which is a precursor of polyimide in the present invention are described.

Examples of the acid anhydrides suitable for preparing the polyimide of the present invention include pyromellitic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 3,4,9,10-perylene-tetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)propane dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)ethane dianhydride, oxydiphthalic dianhydride, bis(3,4-dicarboxyphenyl)sulfonic dianhydride, p-phenylenebis(trimellitic monoester acid anhydride), ethylenebis(trimellitic acid monoester acid anhydride), bisphenol A bis(trimellitic acid monoester acid anhydride) and the like. These compounds can be used alone or in a mixture of any proportion.

Among these, the most suitable acid dianhydride for the polyamide acid composition which is a precursor of polyimide of the present invention, is pyromellitic acid dianhydride. The amount of pyromellitic acid dianhydride is at least 40% by mole, more preferably at least 50% by mole, further preferably at least 70% by mole and most preferably at least 80% by mole.

Examples of the diamine which may suitably be used for the polyamide acid compound which is a precursor of polyimide of the present invention include 4,4'-oxydianiline,

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p-phenylenediamine, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenylmethane, benzidine, 3,3'-dichlorobenzidine, 4,4'-diaminodiphenylsulfide, 3,3'-diaminodiphenylsulfon, 4,4'-diaminodiphenylsulfon, 4,4'-diaminodiphenylether, 3,3'-diaminodiphenylether, 3,4'-diaminodiphenylether, 1,5-diaminonaphthalene, 4,4'-diaminodiphenyldiethylsilane, 4,4'-diaminodiphenylsilane, 4,4'-diaminodiphenylethylphosphineoxide, 4,4'-diaminodiphenyl-N-methylamine, 4,4'-diaminodiphenyl-N-phenylamine, 1,4-diaminobenzene (p-phenylenediamine), 1,3-diaminobenzene, 1,2-diaminobenzene and the like. Among these diamine compounds, preferably 4,4'-oxydianiline and p-phenylenediamine are used in a molar ratio of 9/1 to 4/6, more preferably 8/2 to 5/5. In the case that the molar ratio of these two diamines is out of the range, the coefficient of thermal expansion becomes larger and problems may occur such as the film becomes fragile and the flexural endurance decreases.

In the present invention, means to enhance flexural endurance are controlled by the stiffness value, so both the coefficient of thermal expansion and flexural endurance can be obtained. That is, the coefficient of thermal expansion and flexural endurance can both be obtained by determining the elastic modulus and film thickness so that the stiffness value is 0.4 to 1.2, and by selecting a chemical composition so that the coefficient of thermal expansion is suitable for a flexible printed circuit. Therefore polyamide acid can be synthesized by a common process by suitably selecting a known acid dianhydride and diamine component, preferably from the above-mentioned acid dianhydrides and diamine components, so that the coefficient of thermal expansion becomes 1.0 to 2.5×10^{-5} cm/cm/°C.

Examples of the solvent preferable for synthesizing polyamide acid are amide solvents, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide and N-methyl-2-pyrrolidone and more preferably, N,N-dimethylformamide and N,N-dimethylacetamide can be used.

Also, various organic additives, inorganic fillers and various reinforcement materials can be added when needed.

As for the process of producing polyimide film from the above-mentioned polyamide acid solution, a conventionally known process can be used. Examples of the process include thermal imidization and chemical imidization, and chemical imidization is more preferable in view of thermal dimensional stability and mechanical strength. The chemical cure process is a process of reacting polyamide acid organic solvent solution with a dehydrating agent of which acid anhydrides such as acetic anhydride are typical and an imidization catalyst of which tertiary amines such as isoquinoline, P-picoline and pyridine are typical. Chemical imidization and thermal imidization can be used together. Although the heating conditions may change depending on the type of polyamide acid used and the film thickness, adjusting the heating time and temperature so that the propagation tear strength of the film defined by ASTM D-1938 becomes 140 to 360 g/mm, more preferably 160 to 320 g/mm, most preferably 200 to 300 g/mm is preferable in that the flexural endurance of the film can be enhanced.

In this way, a polyimide film can be obtained which has an average coefficient of thermal expansion at 100° to 200° C. of 1.0 to 2.5×10^{-5} cm/cm/°C., preferably 1.0 to 2.0×10^{-5} cm/cm/°C., more preferably 1.3 to 1.8×10^{-5} cm/cm/°C. and also a stiffness value of 0.4 to 1.2 g/cm, preferably 0.4 to 0.8 g/cm and more preferably 0.5 to 0.7 g/cm.

In the case that the average coefficient of thermal expansion at 100° to 200° C. is out of the above-mentioned range, FPC is likely to warp or curl, which is undesirable. Also, in the case that the stiffness value is below the above-men-

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tioned range, especially when the film is thin, handling the film tends to become difficult due to floppiness, and in the case that the stiffness value is above the range, the flexural endurance tends to decrease. In the case that the stiffness value is within the above-mentioned range, the flexural endurance is enhanced.

The flexible printed circuit of the present invention can be obtained by laminating a conductor on the above-mentioned polyimide film.

Examples of the process for forming a conductor layer on the polyimide film are:

- 1) A process comprising laminating a layer of metal foil such as copper on the polyimide film by methods such as lamination or pressing via an adhesive layer,
- 2) A process comprising forming a conductor layer directly on the polyimide film by plating, vacuum deposition or sputtering
- 3) A process comprising applying polyimide or polyamide acid on Cu foil and then imidizing and/or drying.

In the case that an adhesive agent is used to laminate the conductor on the above-mentioned polyimide film in the flexible printed circuit of the present invention, the adhesive agent used include acrylic type, modified phenolic type, polyimide type and nylon-epoxy type, but is not limited to these examples.

The above-mentioned adhesive agent has an elastic modulus after curing of preferably at least 1 GPa, more preferably at least 1.5 GPa, and further preferably at least 2 GPa. Also, the thickness of the adhesive layer is preferably at most 60 μm , more preferably at most 50 μm and further preferably at most 40 μm . In the case that the elastic modulus and the thickness of the adhesive layer are out of the ranges, the number of flexes tends to decrease.

The thickness of the metal foil used is preferably at most 50 μm , more preferably 35 μm and further preferably 18 μm . In the case that the thickness of the metal foil is above the range, the number of flexes tends to decrease.

Furthermore, a particularly preferable result can be obtained in the case of a combination, in which the thickness of the metal foil is at most 18 μm , the elastic modulus of the adhesive agent is at least 2 GPa, the elastic modulus of the polyimide base film is 400 to 450 kg/mm^2 and the thickness of the polyimide base film is 18 to 22 μm .

In this way, a flexible printed circuit can be obtained in which the number of flexes is at least 10 million times, more preferably at least 20 million times, most preferably at least 40 million times.

The present invention is explained in detail through Examples below, but the present invention is not limited thereto.

Properties were measured in the following manner.

<Coefficient of Thermal Expansion>

Apparatus: TMA8140 made by Rigaku Electronic Corporation

Temperature profile: 20° to 400° C.

Heating rate: 10° C./min

Sample size: 5×20 mm

In order to remove the influence of shrinkage by heat, measurements were repeated twice at the above-mentioned temperature profile and then the average coefficient of thermal expansion at 100° to 200° C. was calculated from the second chart.

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<Stiffness>

Measurements were carried out using a loop stiffness tester made by Toyo Seiki Works Co., Ltd by a sample width of 10 mm, a loop length of 50 mm and a squash distance of 10 mm.

<Film Thickness>

The film obtained is randomly cut out into the size of a sample for a flexural endurance experiment (180×25 mm) defined by JPCA-FC01 and the thickness was measured at ten points in equal intervals in the longitudinal direction from the central area by a contact thickness meter. The average of the obtained measured value X_{ave} was assumed to be the film thickness.

<Propagation Tear Strength of the Film>

The propagation tear strength (g/mm) of the obtained film was measured according to ASTM D-1938.

<Number of Flexes>

A specimen was prepared according to JPCA-FC01. A FPC bending testing device "SEK-31B4" made by Shin-Etsu Engineering KK was used as the testing device and the sample was placed with the cover lay film side upward and measured under conditions of a curvature radius of 0.25 mm, stroke width of 15 mm, testing rate of 1500 rotations/minute and supply current of 1 mA. When the resistance value became 150% of the initial resistance value, it was determined that disconnection had occurred and value of less than 1 million was rounded off and the value was assumed to be the number of flexes.

REFERENCE EXAMPLE 1

Preparation of FPC

A copper-clad laminate was obtained by laminating rolled copper foil to a base film using an acrylic adhesive (Pyralux available from Dupont Co., Ltd., elastic modulus 2.3 GPa) (15 μm thickness). A circuit pattern was formed on the copper layer of the copper-clad laminate by etching according to JPCA-FC01. Then, a cover lay obtained by applying the above adhesive (35 μm thickness) on the exact same film as the base film was placed on the above copper-clad laminate having a circuit pattern and a flexible printed circuit (FPC) was obtained.

EXAMPLES 1, 2, 5 AND 6

A curing agent comprising 20 g of acetic anhydride and 10 g of isoquinoline was mixed to 100 g of a 18% by weight DMF solution of polyamide acid synthesized using pyromellitic dianhydride, 4,4'-oxydianiline and p-phenylenediamine in a mole ratio of 4/3/1. After stirring and defoaming by centrifugation, the mixture was applied by flow casting onto aluminum foil. Stirring and defoaming were conducted while cooling to 0° C. The laminate of the aluminum foil and polyamide acid solution was heated at 120° C. for 150 seconds and a gel film having self supportiveness was obtained. The gel film was peeled from the aluminum foil and fixed in a frame. The gel film was heated at 300° C., 400° C. and 500° C. respectively for 30 seconds and a polyimide film having an average coefficient of thermal expansion at 100° to 200° C. of $1.6 \times 10^{-5} \text{ cm/cm}^\circ \text{C.}$ was

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prepared. Using this film, a FPC was obtained according to Reference Example 1. The properties of the film and the FPC are shown in Table 1.

EXAMPLES 3, 4, 7 AND 8

A curing agent comprising 20 g of acetic anhydride and 10 g of isoquinoline was mixed to 100 g of a 18% by weight DMF solution of polyamide acid synthesized using pyromellitic dianhydride, 4,4'-oxydianiline and p-phenylenediamine in a mole ratio of 3/2/1. After stirring and defoaming by centrifugation, the mixture was applied by flow casting onto aluminum foil. Stirring and defoaming were conducted while cooling to 0° C. The laminate of the aluminum foil and polyamide acid solution was heated at 120° C. for 150 seconds and a gel film having self supportiveness was obtained. The gel film was peeled from the aluminum foil and fixed in a frame. The gel film was heated at 300° C., 400° C. and 500° C. respectively for 30 seconds and a polyimide film having an average coefficient of thermal expansion at 100° to 200° C. of 1.3×10^{-5} cm/cm/° C. was prepared. Using this film, a FPC was obtained according to Reference Example 1. The properties of the film and the FPC are shown in Table 1.

EXAMPLE 9

A FPC was obtained from the polyimide film prepared in Example 1 in the same manner as in Reference Example 1 except that a modified phenolic adhesive (9Y601 available from Kanebo NSC Co., Ltd, elastic modulus 8.4 GPa) was used instead of the acrylic adhesive. The properties of the film and the FPC are shown in Table 1.

EXAMPLE 10

A FPC was obtained from the polyimide film prepared in Example 3 in the same manner as in Reference Example 1 except that a modified phenolic adhesive (9Y601 available from Kanebo NSC Co., Ltd, elastic modulus 8.4 GPa) was

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used instead of the acrylic adhesive. The properties of the film and the FPC are shown in Table 1.

EXAMPLE 11

A polyimide film and FPC were obtained in the same manner as in Example 5 except that the gel film was heated at 300° C., 400° C. and 520° C. respectively for 30 seconds.

EXAMPLE 12

A polyimide film and FPC were obtained in the same manner as in Example 7 except that the gel film was heated at 300° C., 400° C. and 520° C. respectively for 30 seconds.

COMPARATIVE EXAMPLE 1

A curing agent comprising 20 g of acetic anhydride and 10 g of isoquinoline was mixed to 100 g of a 18% by weight DMF solution of polyamide acid synthesized using pyromellitic dianhydride and 4,4'-oxydianiline in a mole ratio of 1/1. After stirring and defoaming by centrifugation, the mixture was applied by flow casting onto aluminum foil. Stirring and defoaming were conducted while cooling to 0° C. The laminate of the aluminum foil and polyamide acid solution was heated at 120° C. for 150 seconds and a gel film having self supportiveness was obtained. The gel film was peeled from the aluminum foil and fixed in a frame. The gel film was heated at 300° C., 400° C. and 500° C. respectively for 30 seconds and a polyimide film having an average coefficient of thermal expansion at 100° to 200° C. of 3.1×10^{-5} cm/cm/° C. was prepared. Using this film, a FPC was obtained according to Reference Example 1. The properties of the film and the FPC are shown in Table 1.

COMPARATIVE EXAMPLE 2

A polyimide film was prepared in the same manner as in Examples 1 and 2 except that the flow casting thickness was changed. Using this film, a FPC was obtained according to Reference Example 1. The properties of the film and the FPC are shown in Table 1.

TABLE 1

	Base Film					FPC					
	X _{ave} (μm)	X _{max} (μm)	X _{min} (μm)	a	Propagation tear strength (g/mm)	Elastic modulus (kg/mm ²)	Loop stiffness (g/cm)	Ease in handling film when processing	Copper foil thickness (μm)	Number of flexes (10,000 times)	Appearance
Ex. 1	21	22	20	0.095	240	420	0.7	good	35	1800	good
Ex. 2	21	23	20	0.14	240	420	0.7	good	18	3200	good
Ex. 3	21	22	20	0.095	220	467	0.8	good	35	1900	good
Ex. 4	21	22	19	0.14	220	467	0.8	good	18	3500	good
Ex. 5	18	20	17	0.17	220	420	0.5	good	35	2100	good
Ex. 6	18	20	17	0.17	220	420	0.5	good	18	>4000	good
Ex. 7	18	19	17	0.11	200	467	0.5	good	35	2300	good
Ex. 8	18	18	17	0.056	200	467	0.5	good	18	>4000	good
Ex. 9	21	22	20	0.095	240	420	0.7	good	18	>4000	good
Ex. 10	21	23	20	0.14	220	467	0.8	good	18	>4000	good
Ex. 11	18	19	17	0.11	190	430	0.5	good	35	1800	good
Ex. 12	18	20	17	0.17	180	470	0.5	good	35	2000	good
Com. Ex. 1	20	22	17	0.25	260	320	0.3	bad	35	1300	warpage
Com. Ex. 2	30	33	28	0.17	290	425	1.9	good	35	800	good

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INDUSTRIAL APPLICABILITY

The present invention provides a flexible printed circuit which has excellent thermal dimensional stability and flexural endurance and is free from curl, torsion and warpage due to temperature change, and a base film thereof. 5

The invention claimed is:

1. A polyimide film for flexible printed circuit, having an average coefficient of thermal expansion of 1.0×10^{-5} to 2.5×10^{-5} cm/cm/° C. in temperature range of 100° C. to 200° C. and a stiffness value of 0.4 to 1.2 g/cm where the polyimide is obtained from diamine containing 4,4'-oxydianiline and paraphenylenediamine in a mole ratio of 9/1 to 4/6. 10

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2. A flexible printed circuit comprising an adhesive layer and/or a conductor layer and an insulation material, wherein the polyimide film of claim 1 is used as said insulation material.

3. The flexible printed circuit of claim 2 having a number of flexes of at least 10 million times.

4. A flexible printed circuit comprising an adhesive layer and/or a conductor layer and an insulation material, wherein the polyimide film of claim 1 is used as said insulation material.

5. The flexible printed circuit of claim 4 having a number of flexes of at least 10 million times.

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EXHIBIT B

US007691961B2

(12) **United States Patent**
Fujihara et al.(10) **Patent No.:** **US 7,691,961 B2**
(45) **Date of Patent:** **Apr. 6, 2010**(54) **POLYIMIDE FILM AND USE THEREOF**

2004/0097694 A1 * 5/2004 Fujihara et al. 528/335

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Primary Examiner—James Seidleck*Assistant Examiner*—Gregory Listvoyb(74) *Attorney, Agent, or Firm*—Westerman, Hattori, Daniels & Adrian, LLP**Related U.S. Application Data**

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See application file for complete search history.

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(57) **ABSTRACT**

A polyimide film in which the dimensional change is reduced when it has undergone a step of laminating a metal on the polyimide film or a step of etching the metal layer to form wiring, and the rate of dimensional change can be stabilized across the entire width is provided. The object can be solved by a polyimide film produced by a continuous process, wherein when a coefficient of linear expansion a in a direction of the molecular orientation axis and a coefficient of linear expansion b in a direction perpendicular to the molecular orientation axis are measured in the temperature range of 100° C. to 200° C., a and b satisfy a particular relationship across the entire width, or a polyimide film produced by a continuous process, wherein when a tear propagation resistance c in the direction of the molecular orientation axis and a tear propagation resistance d in the direction perpendicular to the molecular orientation axis are measured, c and d satisfy a particular relationship across the entire width.

20 Claims, 7 Drawing Sheets

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FIG. 1

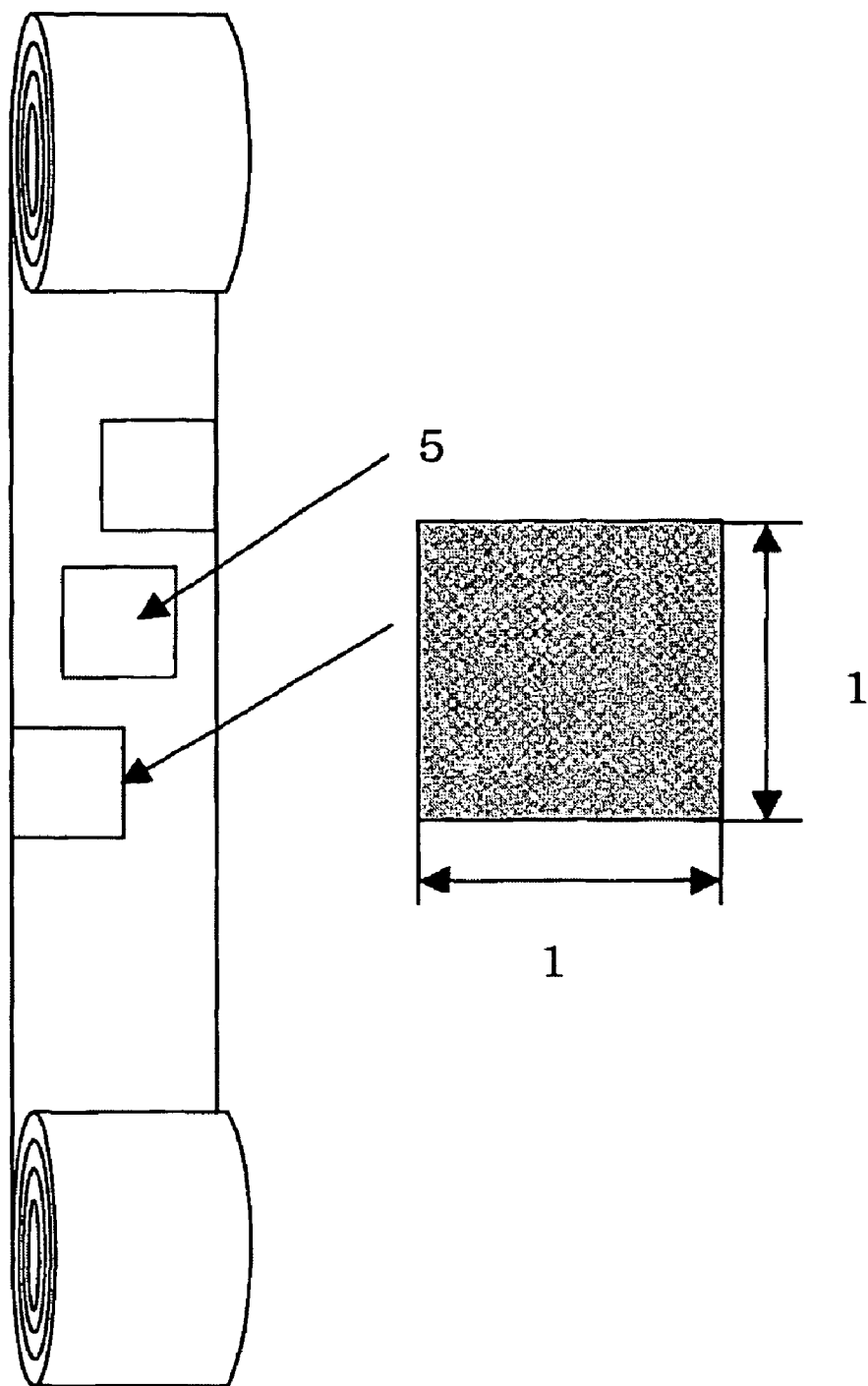
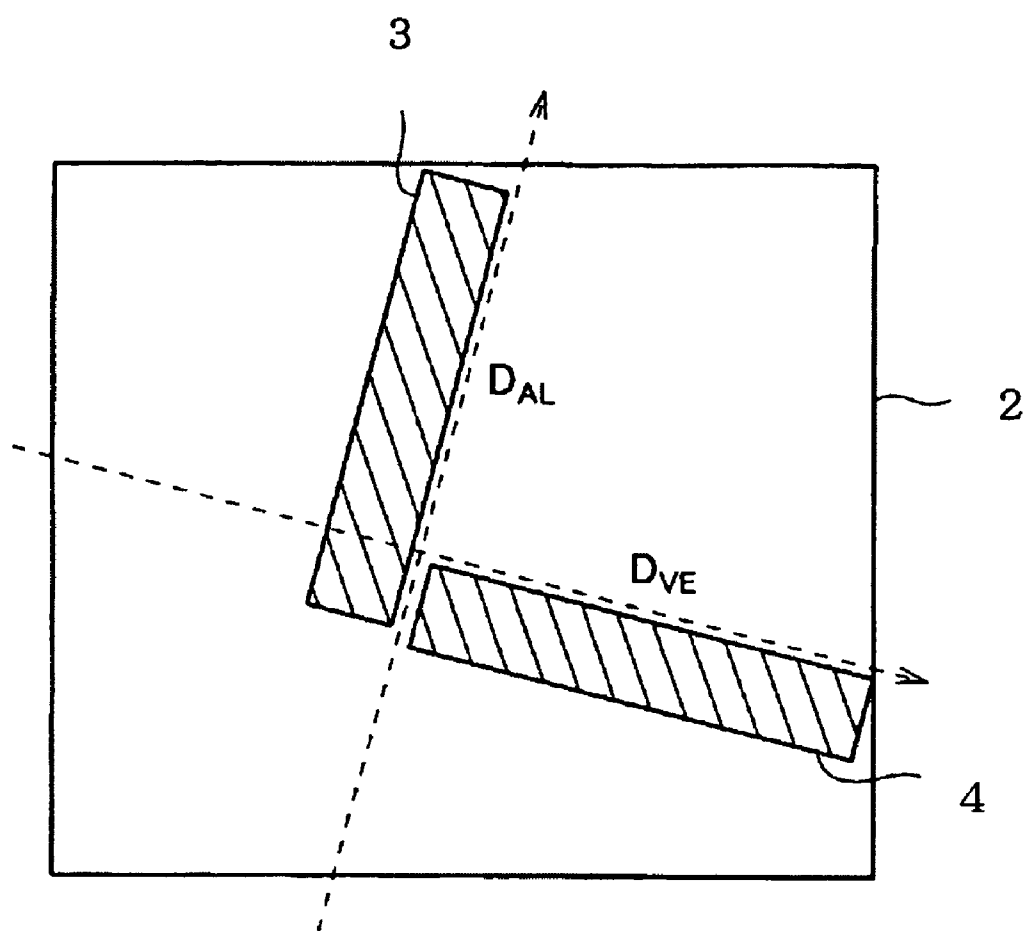


FIG. 2



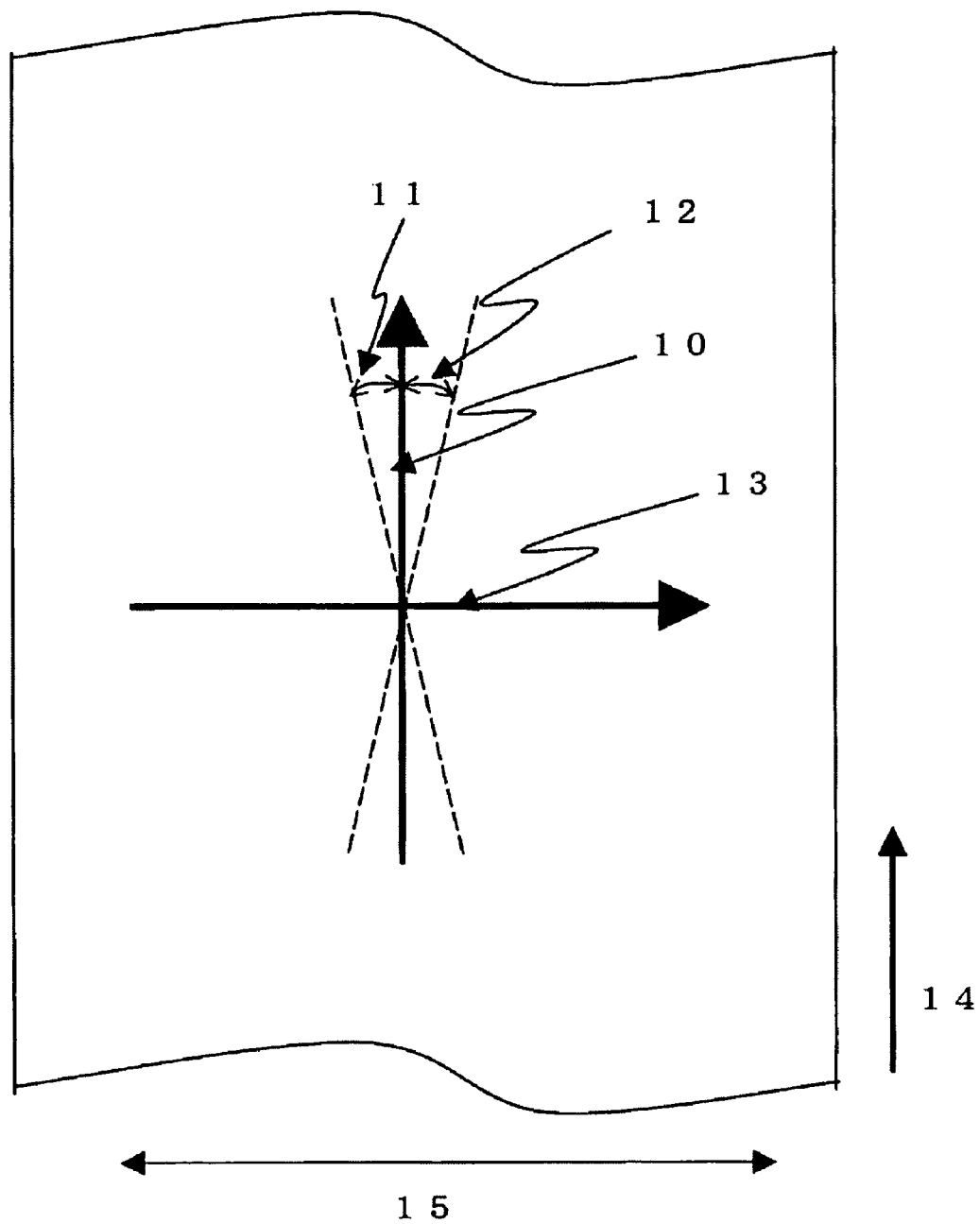
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FIG. 3



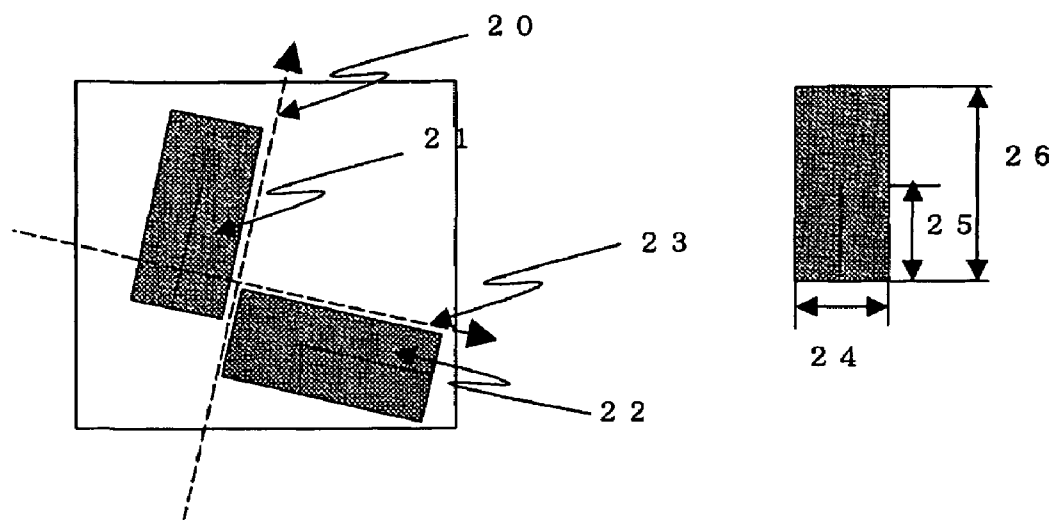
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FIG. 4



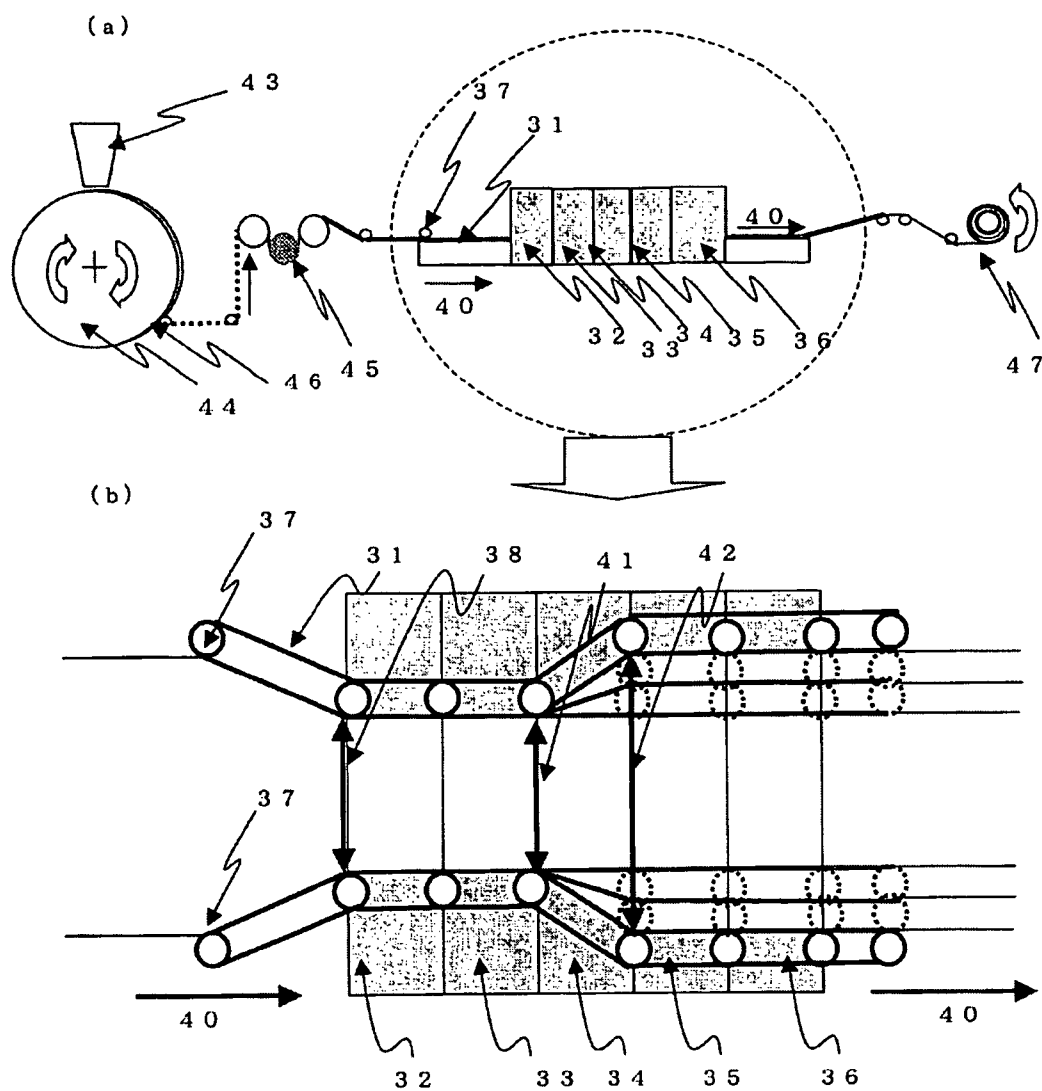
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FIG. 5



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FIG. 6

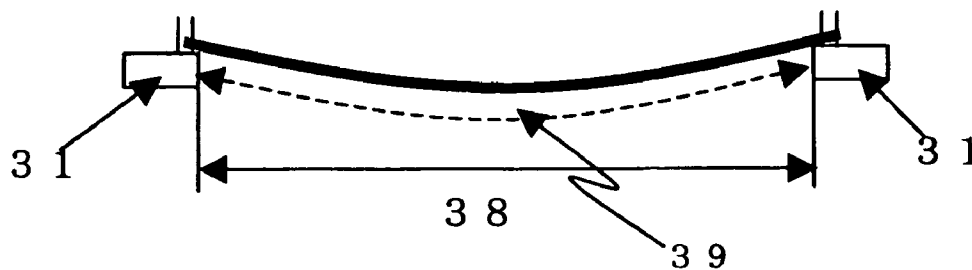


FIG. 7

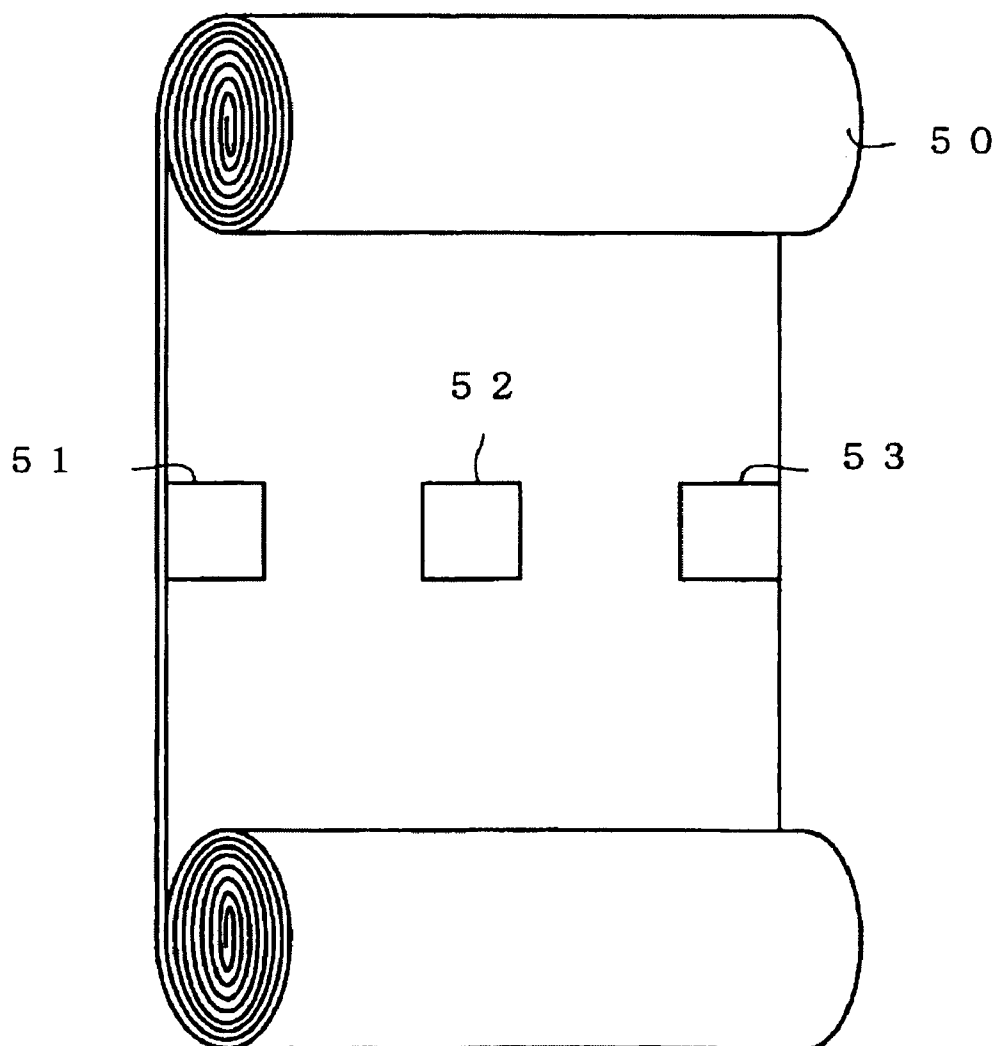
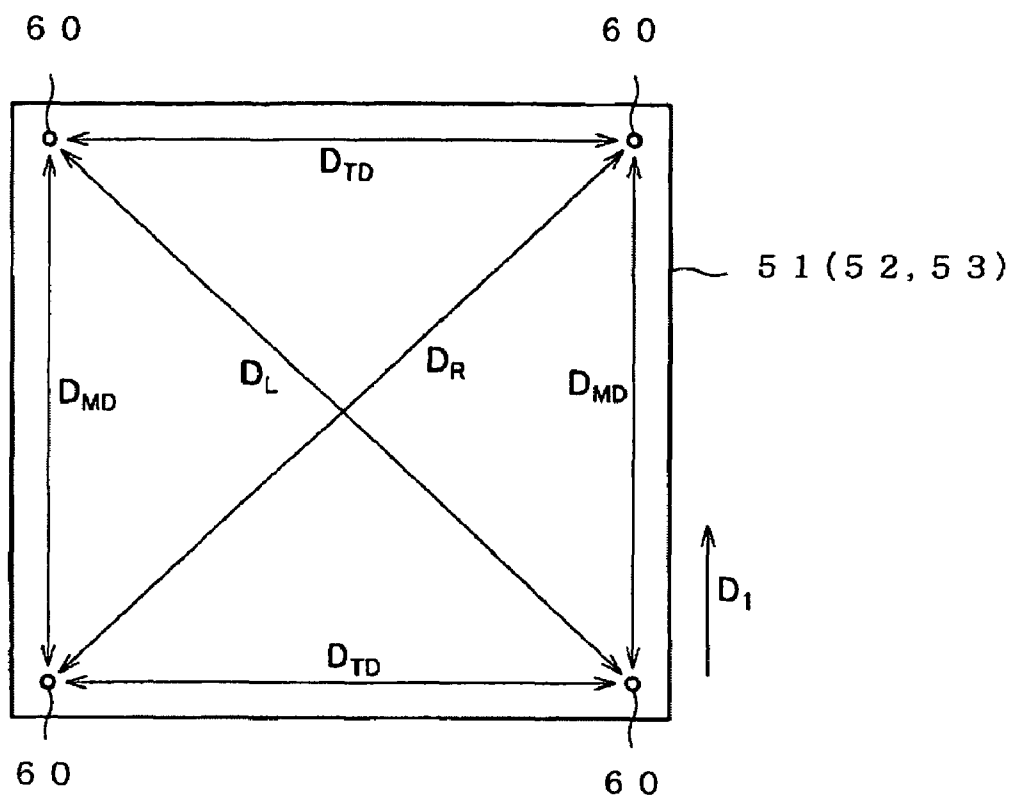


FIG. 8



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POLYIMIDE FILM AND USE THEREOF

RELATED APPLICATION

This application is a Continuation-in-Part of PCT application PCT/JP2005/004282 filed on Mar. 11, 2005, claiming priority based on Japanese Application No. 2004-0473558 and 2004-094901 filed on Mar. 15, 2004 and Mar. 29, 2004 respectively, the contents of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

The present invention relates to a polyimide film suitable for use in flexible printed circuit boards, tapes for tape automated bonding (TAB), substrates for electrical and electronic devices such as a substrate for a solar cell, high-density recording media, and magnetic recording media, and use thereof. More specifically, the present invention relates to a polyimide film in which the rate of dimensional change is reduced when it has undergone a step of forming a metal layer, in particular, a step of laminating a metal foil under heating or a step of etching the metal layer, and physical property values (rate of dimensional change) can be stabilized across the entire width of the film.

BACKGROUND ART

In the technical field of electronics, demand for high-density mounting has been increasing. Accordingly, in the technical field using a flexible printed circuit board (hereinafter referred to as "FPC"), physical properties etc. that are suitable for the high-density mounting have been desired.

A process of producing the FPC is broadly divided into (1) a step of laminating a metal onto a base film (hereinafter referred to as "metal lamination step") and (2) a step of forming wiring with a desired pattern on the metal surface (hereinafter referred to as "wiring formation step"). In particular, in the process of producing the FPC for high-density mounting, a small dimensional change of the base film is desired.

In the metal lamination step and the wiring formation step, the dimensional change of the base film is particularly increased in the following stages. (1) In the metal lamination step, before and after a stage of laminating a metal while heating the base film. (2) In the wiring formation step, before and after etching for patterning the metal. Therefore, when the FPC for high-density mounting is produced, desirably, the dimensional change of the base film is small before and after these stages.

In the production of FPCS, a metal layer is laminated by a roll-to-roll processing of a base film with a large width. Therefore, it is desired that the physical properties of the base film be stable across the entire width (the entire width direction), that is, the rate of dimensional change be stable across the entire width of the base film.

A polyimide film containing a polyimide resin as a main component is suitably used as the base film. In the polyimide film used as the base film, various techniques have been proposed in order to control the rate of dimensional change.

For example, Patent Document 1 discloses a polyimide film produced by appropriately selecting monomer materials in which an average coefficient of linear expansion is about 1 to 25 ppm/° C. in the temperature range of about 50° C. to 300° C. and a coefficient of linear expansion ratio (MD/TD) in the machine direction (MD) and the transverse direction (TD) of the polyimide film is about 1/5 to 4 (see p. 1, claim 1;

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p. 2, lower left, lines 4 to 14; p. 3, lower right, lines 1 to 10; and the like of the document). In Patent Document 1, the dimensional stability of the film itself during heating is improved.

As a technique for controlling the dimensional changes by stretching a polyimide film in at least one direction, Patent Document 2 proposes a method of swelling a precursor film of polyimide containing a residual solvent with a swelling agent, and then stretching the film in at least a uniaxial direction (see claim 1, paragraphs [0007], [0028], and the like of the document). Patent Document 3 proposes a method of swelling a gel film of a polyimide-amic acid ester copolymer with a solvent, and then stretching the film under heating (see paragraphs [0035] to [0038], and the like of the document). Patent Document 4 proposes a method of biaxially stretching a gel film under a specified degree of swelling, thereby controlling the thermal coefficient of linear expansion in the in-plane direction to be 10 ppm/° C. or less (see claim 3, paragraphs [0015], [0023], [0042], [0045] and the like of the document).

Patent Document 5 proposes a method of stretching a resin film (polyimide film) used as a base film layer of a tape for TAB in a uniaxial direction at a ratio in a predetermined range on the basis of the glass transition temperature, and then annealing the film (see claims 4 and 5, paragraphs [0017], [0041], and the like of the document). Patent Document 6 proposes a method of stretching a polyimide film at a ratio of 1.0 to 1.5 in the MD direction and at a ratio of 0.5 to 0.99 in the TD direction in the production of the polyimide film (see paragraphs [0021], [0044], and the like of the document). Patent Document 7 proposes a method of applying a zone stretching (a method of stretching in which molecular chains of a raw film are aligned so as to agglomerate in a reed blind shape) on a polyimide film at a temperature of 250° C. or higher (see p. 1, claim 1; p. 2, upper left, line 15 to upper right, line 6; p. 2, lower left, line 7 to p. 3, upper right line 4; and the like of the document).

Furthermore, as a technique for controlling the dimensional changes by specifying a condition during drying (during imidization) using a tenter furnace (a furnace in which both ends in the width direction of a film are fixed to perform heating) (for convenience, referred to as "tenter process technique"), Patent Document 8 proposes a method of sequentially decreasing the distance between the fixed ends of a film in the first half of a heating furnace, and sequentially increasing the distance in the second half of the heating furnace in producing a polyimide film by a tenter process (see paragraphs [0005], [0032], and the like of the document). Patent Document 9 proposes a method of producing a polyimide film wherein when a self-supporting film is being carried in a tenter furnace while both ends of the film are held, the width of the film between the gripping positions is gradually decreased to 0.95 times that of the gripping part during a step of increasing the temperature to 300° C. at which the shrinkage due to drying is almost completed. Thereby, a polyimide film having a coefficient of linear expansion (TD) of 17 to 24 ppm/° C. in the temperature range from 50° C. to 200° C. and a tensile modulus (TD) of 700 kgf/mm² or more is produced (see paragraphs [0020], [0021], and the like of the document).

However, none of Patent Documents 1 to 9 describes a film disclosed in the present invention in which the coefficient of linear expansion in a direction of the molecular orientation axis and the coefficient of linear expansion in a direction perpendicular to the molecular orientation axis (for convenience, this direction may be referred to as "a perpendicular direction") satisfy a particular relationship. For example, in some cases, it is difficult to reduce the rate of dimensional change when a metal is continuously laminated on a film or

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when wiring is formed by etching the metal layer. Furthermore, the amounts of dimensional change are different between an end of the polyimide film and the central portion thereof. Consequently, it may be difficult to stabilize the rate of dimensional change across the entire width of the film.

On the other hand, Patent Documents 10 to 14 disclose polyimide films in which the composition, the thickness, the tensile modulus, and the tear propagation resistance are specified.

However, none of Patent Documents 10 to 14 describes a film disclosed in the present invention in which the tear propagation resistance *c* in a direction of the molecular orientation axis and the tear propagation resistance *d* in a direction perpendicular to the molecular orientation axis satisfy a particular relationship. In addition, these polyimide films are aimed at improving the handleability during mounting on a substrate or the like and the punchability. Therefore, for example, when a metal is continuously laminated on a film or when wiring is formed by etching the metal layer, the generation of dimensional changes may not be satisfactorily suppressed. Furthermore, the amounts of dimensional change are different between an end portion of the polyimide film and the central portion thereof. Consequently, it may be difficult to stabilize the rate of dimensional change across the entire width of the film.

Polyimide films are generally produced by a tenter furnace process in which ends of the film are gripped with clips or pin seats, and the film is transferred through a high-temperature furnace to bake the film. However, when a polyimide film is produced by the tenter furnace process, the same phenomenon as that caused by anisotropy of molecular orientation (generally referred to as "bowing phenomenon") described in, for example, Non-Patent Documents 1 and 2 occurs in the production process of the polyimide film. Consequently, the anisotropy of molecular orientation is generated at the ends of the film (in particular, a part located within about 50 cm from a film-gripping device). When such anisotropy is exhibited, for example, a difference in coefficient of linear expansion and a difference in dimensional change are generated in the width direction of the film.

The present inventors have found that when the ratio between the coefficient of linear expansion in a direction of the molecular orientation axis of a polyimide film and the coefficient of linear expansion in a direction perpendicular to the molecular orientation axis thereof satisfies a particular relationship, the rate of dimensional change in the case where a metal is continuously laminated on the film or wiring is formed by etching the metal layer is small, or the rate of dimensional change can be stabilized across the entire width of the film.

Furthermore, the present inventors have found that, in a polyimide film in which the ratio between the tear propagation resistance *c* in a direction of the molecular orientation axis of the polyimide film and the tear propagation resistance *d* in a direction perpendicular to the molecular orientation axis thereof (for convenience, this direction may be referred to as "a perpendicular direction") is within a specific range, the rate of dimensional change in the case where a metal is continuously laminated on the film or wiring is formed by etching the metal layer is small, and the rate of dimensional change can be stabilized across the entire width of the film.

Patent Document 1: Japanese Unexamined Patent Application Publication No. 61-264028 (Publication Date: Nov. 21, 1986)

Patent Document 2: Japanese Unexamined Patent Application Publication No. 2002-1804 (Publication Date: Jan. 8, 2002)

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Patent Document 3: Japanese Unexamined Patent Application Publication No. 2003-128811 (Publication Date: May 8, 2003)

Patent Document 4: Japanese Unexamined Patent Application Publication No. 2003-145561 (Publication Date: May 20, 2003)

Patent Document 5: Japanese Unexamined Patent Application Publication No. 8-174695 (Publication Date: Jul. 9, 1996)

Patent Document 6: Japanese Unexamined Patent Application Publication No. 11-156936 (Publication Date: Jun. 15, 1999)

Patent Document 7: Japanese Unexamined Patent Application Publication No. 63-197628 (Publication Date: Aug. 16, 1998)

Patent Document 8: Japanese Unexamined Patent Application Publication No. 2000-290401 (Publication Date: Oct. 17, 2000)

Patent Document 9: Japanese Unexamined Patent Application Publication No. 2002-179821 (Publication Date: Jun. 26, 2002)

Patent Document 10: Japanese Unexamined Patent Application Publication No. 11-246685 0009

Patent Document 11: Japanese Unexamined Patent Application Publication No. 2000-244083 0010 and 0011

Patent Document 12: Japanese Unexamined Patent Application Publication No. 2000-198969 0009 and 0010

Patent Document 13: Japanese Unexamined Patent Application Publication No. 2000-208563 0008 and 0009

Patent Document 14: Japanese Unexamined Patent Application Publication No. 2000-208564 0008 and 0009

Non-Patent Document 1: Kunisuke Sakamoto, *Kobunshi Ronbunshu* (Japanese Journal of Polymer Science and Technology) Vol. 48, No. 11, pp. 671-678 (1991)

Non-Patent Document 2: Chisato Nonomura et al., *Journal Seikei-Kakou*, Vol. 4, No. 5, pp. 312 to 317 (1992)

DISCLOSURE OF INVENTION

Problems to be Solved by the Invention

In the known polyimide films, it may be difficult to reduce dimensional changes when the films have undergone a step of laminating a metal thereon or a step of forming wiring by etching the metal layer, and to stabilize the rate of dimensional change across the entire width of the film. In addition, a polyimide film that undergoes a small dimensional change before and after a step of producing an FPC using the polyimide film as a base film, for example, a step of laminating a metal on the base film, or a step of forming wiring with a desired pattern on the surface of the metal, in particular, the polyimide film that has a stable rate of dimensional change across the entire width of the film when the polyimide film is produced by laminating the metal by a roll-to-roll processing of the base film with a large width has not yet been provided. In order to solve this problem, the present inventors have conducted intensive studies and have made the present invention.

Means for Solving the Problems

The present invention can solve the above problem by means of the following novel polyimide films and laminates including the same.

1) A polyimide film produced by a continuous process, wherein when a coefficient of linear expansion *a* in a direction of the molecular orientation axis and a coefficient of

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linear expansion b in a direction perpendicular to the molecular orientation axis are measured in the temperature range of 100° C. to 200° C., a coefficient of linear expansion ratio A represented by equation (1):

$$A=1+\{(b-a)/(b+a)\} \times 2 \quad (1)$$

is in the range of 1.01 to 3.00 across the entire width.

- 2) The polyimide film according to 1) above, wherein the difference between the maximum A_{MAX} and the minimum A_{MIN} of the coefficient of linear expansion ratio A is 0.30 or less.
- 3) The polyimide film according to 1) or 2) above, wherein the difference between the maximum and the minimum of the molecular orientation angle of the polyimide is 40° or less across the entire width.
- 4) The polyimide film according to any one of 1) to 3) above, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle is within $0 \pm 20^\circ$.
- 5) The polyimide film according to any one of 1) to 4) above, wherein the average coefficient of linear expansion in the temperature range of 100° C. to 200° C. is in the range of 5.0 to 25.0 ppm/° C.
- 6) A laminate including the polyimide film according to any one of 1) to 5) above.
- 7) The laminate according to 6) above, further including at least a metal layer.
- 8) A flexible printed circuit board including the polyimide film according to any one of 1) to 5) above as a base film.
- 9) A polyimide film produced by a continuous process, wherein when a tear propagation resistance c in a direction of the molecular orientation axis and a tear propagation resistance d in a direction perpendicular to the molecular orientation axis are measured, the tear propagation resistance ratio d/c is in the range of 1.01 to 1.20 and the difference between the maximum and the minimum of the tear propagation resistance ratio d/c is 0.10 or less across the entire width.
- 10) The polyimide film according to 9) above, wherein the difference between the maximum and the minimum of the molecular orientation angle of the polyimide film is 40° or less across the entire width.
- 11) The polyimide film according to 9) or 10) above, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle of the polyimide film is within $0 \pm 20^\circ$ across the entire width.
- 12) A laminate including the polyimide film according to any one of 9) to 11) above.
- 13) The laminate according to 12) above, further including at least a metal layer.
- 14) A flexible printed circuit board including the polyimide film according to any one of 9) to 11) above as a base film.

EFFECT OF THE INVENTION

A polyimide film of the present invention is a polyimide film produced by a continuous process wherein when the coefficient of linear expansion a in a direction of the molecular orientation axis and the coefficient of linear expansion b in a direction perpendicular to the molecular orientation axis are measured in the temperature range of 100° C. to 200° C., these coefficients of linear expansion satisfy a particular relationship across the entire width.

A polyimide film of the present invention is a polyimide film wherein when the tear propagation resistance c in a

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direction of the molecular orientation axis and the tear propagation resistance d in a direction perpendicular to the molecular orientation axis are measured, a tear propagation resistance ratio d/c is in the range of 1.01 to 1.20.

According to these films, for example, when the polyimide film is used as a base film of an FPC, the rate of dimensional change generated before and after the lamination of a metal layer and an etching process thereof can be reduced, and the rate of dimensional change can be stabilized across the entire width. Consequently, for example, these films provide an advantage that a high-quality FPC permitting high-density mounting can be provided.

BEST MODE FOR CARRYING OUT THE INVENTION

In embodiments, the present invention will be described in detail, in the order of the outline of a polyimide film of the present invention, a representative example of a method of producing the polyimide film, and the use of the polyimide film.

(I) Polyimide Film of the Present Invention

The polyimide film of the present invention is suitably used as a base film of an FPC and has a reduced rate of dimensional change before and after the lamination of a metal layer and the etching process. In particular, in the polyimide film, the rate of dimensional change is stabilized across the entire width.

In general, in producing FPCs, rates of dimensional change are measured in advance before and after the etching process of a metal-clad laminate (hereinafter referred to as "CCL") prepared by laminating a metal and before and after heat treatment, and a correction coefficient is determined on the basis of the values.

When the rate of dimensional change of the CCL is stabilized across the entire width, the amount of dimensional change can be estimated using a single correction coefficient across the entire width of the CCL. Therefore, in the above-described process for producing an FPC, the amount of dimensional change after a step of heating and the amount of dimensional change after etching can be estimated in advance. Consequently, for example, when metal wiring is formed on a metal layer of the CCL, the pattern wiring can be easily formed. Accordingly, the production yield is improved and the reliability of the connection of the pattern wiring can also be improved, which can markedly contribute to the improvement in, for example, the quality and the yield of the FPC.

On the other hand, when the rate of dimensional change varies depending on the positions of the film, it is difficult to estimate the amount of dimensional change using a single correction coefficient to produce the FPC. Therefore, only a part having a stable rate of dimensional change of the CCL must be selected for use, or a part having a stable physical properties of the polyimide film that particularly affect the rate of dimensional change of the CCL must be selected for use. Since the disposal part increases, this method has a low production yield.

In order to control the rate of dimensional change and the variation thereof across the entire width to low values even after the above process, at least a coefficient of linear expansion ratio A represented by equation (1):

$$A=1+\{(b-a)/(b+a)\} \times 2 \quad (1)$$

is specified within a predetermined range across the entire width of the polyimide film. Preferably, the polyimide film satisfies a condition that the upper limit of the difference

between the maximum and the minimum of the coefficient of linear expansion ratio A is specified. More preferably, the polyimide film satisfies a condition that the molecular orientation angle across the entire width of the polyimide film is specified.

According to another embodiment of the present invention, the polyimide film satisfies the conditions that when the tear propagation resistance c in a direction of the molecular orientation axis and the tear propagation resistance d in a direction perpendicular to the molecular orientation axis are measured, a tear propagation resistance ratio d/c is specified within a predetermined range, and that the upper limit of the difference between the maximum and the minimum of the tear propagation resistance ratio is specified, and preferably satisfies the condition that the molecular orientation angle across the entire width of the polyimide film is specified.

The polyimide film thus obtained can exhibit excellent dimensional stability (refer to examples, in particular, the rate of dimensional change described below), and can be suitably used as a base film of an FPC or the like.

Furthermore, in the polyimide film of the present invention, it is also possible to control the rate of dimensional change to be a low value before and after compression bonding performed by a hot roll lamination method in which the polyimide film and a metal foil are continuously bonded by thermocompression bonding with a bonding material therebetween. When the metal foil is bonded by the hot roll lamination method, the material is often brought in a heating environment under applied tension. Therefore, this may cause the problem of the rate of dimensional change. However, the use of the specific polyimide film of the present invention can reduce the rate of dimensional change and can stabilize the rate of dimensional change across the entire width.

These conditions will now be specifically described.

<Coefficient of Linear Expansion Ratio A and Difference A_{DIF} in Coefficient of Linear Expansion Ratio>

The polyimide film of the present invention is continuously produced. In this case, a coefficient of linear expansion ratio A represented by equation (1):

$$A = 1 + \{(b-a)/(b+a)\} \times 2 \quad (1)$$

satisfies $1.01 \leq A \leq 3.00$ across the entire width of the polyimide film. Furthermore, the difference between the maximum of the coefficient of linear expansion ratio A and the minimum thereof (difference A_{DIF} in coefficient of linear expansion ratio) preferably satisfies $A_{DIF} \leq 0.30$.

In the polyimide film of the present invention, the term "entire width" means the entire part in the direction (width direction, TD direction) perpendicular to the transferring direction (MD direction) in which the film is continuously produced. The specific methods of measuring the physical property values (coefficient of linear expansion etc.) across the entire width are not particularly limited. However, as described in examples below, the physical property values are measured at three points of both end portions and the central portion along the TD direction of the polyimide film, and these measured values may be compared or utilized.

In general, when a film (polyimide film) is produced by a tenter furnace process, since a stress due to the shrinkage of the film concentrates on the ends of the film, the physical property values at the ends may be significantly different from that at the central portion. Therefore, it is reasonable to consider that the physical property value of the entire width of the film is expressed by measuring the respective physical property values at both end portions and the central portion.

In the polyimide film produced by a continuous process in the present invention, when the polyimide film has a length of 200 mm or more in the width direction, and a length of 20 mm or more in the longitudinal direction, the advantages of the invention can be markedly achieved. The polyimide film produced by a continuous process in the present invention includes a film that is produced by slitting a film having the above width into certain dimensions in the width direction and the longitudinal direction of the film.

The molecular orientation axis represents the direction of the highest degree of molecular orientation in the X-Y plane of the polyimide film wherein the MD direction of the polyimide film is defined as the X-axis and the TD direction thereof is defined as the Y-axis. Any general-purpose measuring device may be used for measuring the molecular orientation axis and the device is not particularly limited. For example, in the present invention, as described in examples below, the measurement can be performed with a molecular orientation analyzer, e.g., trade name: MOA 2012A or trade name: MOA 6015, manufactured by Oji Scientific Instruments.

In order to measure the coefficient of linear expansion a in a direction of the molecular orientation axis and the coefficient of linear expansion b in a direction perpendicular to the molecular orientation axis of the polyimide film in the present invention, first, the molecular orientation axis is determined with the device. In the measurement of the molecular orientation axis, measurement samples (40 mm×40 mm) are prepared from both end portions and the central portion of the width direction of the polyimide film, and the molecular orientation axes of the measurement samples are measured. When the width of the sample is small, preferably, respective samples are obtained so that the sampling position is shifted in the MD direction. For example, when the film width is 100 mm, sampling is preferably performed so that the sampling position is shifted in the MD direction as shown in FIG. 1.

In the present invention, the coefficients of linear expansion of the polyimide film are measured with respect to both the direction of the molecular orientation axis and the direction perpendicular to the molecular orientation axis (referred to as "a perpendicular direction" for convenience). A specific measuring method will be described. The angle of the molecular orientation axis is measured as described above, and measurement samples are prepared on the basis of the molecular orientation axis. For example, as shown in FIG. 2, reed-shape measurement samples 3 and 4 of a polyimide film 2 are respectively cut out in a direction of the molecular orientation axis (D_{AL} in the figure) and the perpendicular direction (D_{VE}). The size of the measurement samples 3 and 4 is not particularly limited as long as the measurement samples 3 and 4 have a size suitable for the measurement of the coefficient of linear expansion.

The thermal expansion coefficients of the measurement samples 3 and 4 thus prepared are measured with a known measurement device. For example, the coefficient of linear expansion is measured with a thermomechanical analyzer (manufactured by Seiko Instruments Inc., trade name: TMA120C) as follows. The sample is first heated from room temperature to 400° C. under a nitrogen stream at a heating rate of 10° C./min. Subsequently, the sample is gradually cooled to room temperature and is heated again from room temperature to 400° C. The thermal expansion coefficient calculated in the temperature range of 100° C. to 200° C. is defined as the coefficient of linear expansion.

In the present invention, the coefficient of linear expansion ratio A of the polyimide film 2 is calculated from the measured coefficients of linear expansion using the following

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equation (1). In equation (1), the coefficient of linear expansion in a direction of the molecular orientation axis is defined as a , and the coefficient of linear expansion in the perpendicular direction is defined as b .

$$A = 1 + \{(b-a)/(b+a)\} \times 2 \quad (1)$$

The coefficient of linear expansion ratio A calculated using equation (1) is preferably in the range of 1.01 to 3.00 ($1.01 \leq A \leq 3.00$), and more preferably in the range of 1.01 to 2.00 ($1.01 \leq A \leq 2.00$). When the coefficient of linear expansion ratio of the polyimide film is within this range, the rate of dimensional change across the entire width can be reduced, and the dimensional stability across the entire width can be satisfactory, in particular, before and after the etching stage in the production of FPCs.

Furthermore, in the present invention, the difference between the maximum (A_{MAX}) and the minimum (A_{MIN}) of the coefficient of linear expansion ratio A across the entire width (difference A_{DIF} in coefficient of linear expansion ratio = $A_{MAX} - A_{MIN}$) is preferably 0.30 or less ($A_{DIF} \leq 0.30$), more preferably 0.25 or less ($A_{DIF} \leq 0.25$), and particularly preferably 0.20 or less ($A_{DIF} \leq 0.20$). A small difference A_{DIF} in coefficient of linear expansion ratio does not cause a problem. On the other hand, in order to realize satisfactory dimensional stability before and after the etching stage in the production of FPCs, the upper limit of the difference A_{DIF} in coefficient of linear expansion ratio is 0.30 or less. Thus, by specifying the difference A_{DIF} in coefficient of linear expansion ratio, the rate of dimensional change can be satisfactorily stabilized across the entire width of the polyimide film.

In the present invention, the molecular orientation axis and the coefficient of linear expansion are measured as described above. The relationship between the above method of preparing samples and the measured values is as follows. Namely, square measurement samples with dimensions of 4×4 cm are prepared from both end portions and the central portion of the polyimide film, and the molecular orientation axis is measured. Since the molecular orientation axis is determined, strip measurement samples are prepared in the direction of the molecular orientation axis and the direction perpendicular to the molecular orientation axis, and the coefficients of linear expansion of the samples are then measured. The coefficient of linear expansion ratio A and the difference A_{DIF} in coefficient of linear expansion ratio are calculated from the coefficients of linear expansion measured as described above.

<Average Coefficient of Linear Expansion C_{LE} >

In the polyimide film of the present invention, in addition to the coefficient of linear expansion ratio A and the difference A_{DIF} in coefficient of linear expansion ratio, an average coefficient of linear expansion C_{LE} is also preferably specified. The coefficient of linear expansion a in a direction of the molecular orientation axis and the coefficient of linear expansion b in the perpendicular direction are measured across the entire width, and the average coefficient of linear expansion C_{LE} is then calculated using the following equation (2). In equation (2), as shown in FIG. 2, the coefficient of linear expansion in the direction of the molecular orientation axis (D_{AL} in the figure) at an end is defined as $C1_{AL}$, the coefficient of linear expansion in the perpendicular direction (D_{VE}) at the end is defined as $C1_{VE}$, the coefficient of linear expansion in the direction of the molecular orientation axis (D_{AL} in the figure) at the center is defined as $C0_{AL}$, the coefficient of linear expansion in the perpendicular direction (D_{VE}) at the center is defined as $C0_{VE}$, the coefficient of linear expansion in the direction of the molecular orientation axis (D_{AL} in the figure)

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at another end is defined as $C2_{AL}$, and the coefficient of linear expansion in the perpendicular direction (D_{VE}) at the other end is defined as $C2_{VE}$.

$$C_{LE} = \{(C1_{AL} + C1_{VE})/2 + (C0_{AL} + C0_{VE})/2 + (C2_{AL} + C2_{VE})/2\} / 3 \quad (2)$$

In particular, when the polyimide film is used as a base film of an FPC, the average coefficient of linear expansion C_{LE} is preferably a value close to the average coefficient of linear expansion (16.3 ppm/° C.) of a metal layer (in particular, a copper layer) in the temperature range of 100° C. to 200° C., or lower than the value. The reason for this is as follows. From the viewpoint that the polyimide film is stretched during heat treatment in the production of FPC, when the average coefficient of linear expansion of the polyimide film is close to the coefficient of linear expansion of the copper layer, the dimensional stability can be naturally improved.

Accordingly, in the polyimide film of the present invention, the average coefficient of linear expansion in the temperature range of 100° C. to 200° C. is preferably in the range of 5.0 to 25.0 ppm/° C., more preferably in the range of 5.5 to 23.0 ppm/° C., and further preferably in the range of 6.0 to 20.0 ppm/° C. When the average coefficient of linear expansion of the polyimide film is within the above range, in the case where an FPC is produced using the polyimide film as a base film, the rate of dimensional change of the base film before and after etching can be reduced.

<Molecular Orientation Angle and Difference in Molecular Orientation Angle>

In the polyimide film of the present invention, in addition to the coefficient of linear expansion ratio A and the difference A_{DIF} in coefficient of linear expansion ratio, a molecular orientation angle across the entire width of the polyimide film is also preferably specified. With respect to the specification of the molecular orientation angle, at least one of the difference between the maximum and the minimum of the molecular orientation angle across the entire width of the polyimide film and a small variation in the molecular orientation angle across the entire width of the polyimide film is specified. This molecular orientation angle means the angle formed by the molecular orientation axis described in the above section <coefficient of linear expansion ratio A and difference A_{DIF} in coefficient of linear expansion ratio>.

First, regarding the difference between the maximum and the minimum of the molecular orientation angle (for convenience, referred to as “difference in molecular orientation angle”), the upper limit of the difference in molecular orientation angle is 40° or less and more preferably 30° or less. In the case where the upper limit of the difference in molecular orientation angle is within the above range, when an FPC is formed with a metal layer, the variation in the rate of dimensional change across the entire width before and after etching can be reduced, thus being preferable. In this case, the direction of the molecular orientation angle is not particularly limited, and may be any direction.

The molecular orientation angle in the present invention means the angle formed between the measured molecular orientation axis and the MD direction. The phrase “the molecular orientation angle of the polyimide film is 0°” means that the direction of the molecular orientation axis is a direction (the same direction as shown by 10 in FIG. 3) parallel to the MD direction (the same direction as shown by 14 in FIG. 3). The term “positive (plus) molecular orientation angle” represents the case where the angle is tilted from the MD direction in the counterclockwise direction (11 in FIG. 3). On the other hand, the term “negative (minus) molecular

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orientation angle" represents the case where the angle is tilted from the MD direction in the clockwise direction (12 in FIG. 3). The difference in molecular orientation angle in the present invention can be measured as follows. First, the molecular orientation angles are measured across the width direction of the film. The difference in molecular orientation angle can be calculated using the following equation (3) from the maximum positive molecular orientation angle and the maximum negative molecular orientation angle. When only positive molecular orientation angles are observed across the width direction, equation (4) is used. When only negative molecular orientation angles are observed across the width direction, equation (5) is used. When the maximum or the minimum of the molecular orientation angle is 0°, the difference in molecular orientation angle can be determined as follows. When 0° is the maximum, the difference in molecular orientation angle is determined by equation (6) using the minimum negative molecular orientation angle. When 0° is the minimum, the difference in molecular orientation angle is determined by equation (7) using the maximum positive molecular orientation angle.

$$\text{Difference in molecular orientation angle} = (\text{positive molecular orientation angle}) - (\text{negative molecular orientation angle}) \quad (3)$$

$$\text{Difference in molecular orientation angle} = (\text{the maximum positive molecular orientation angle}) - (\text{the minimum positive molecular orientation angle}) \quad (4)$$

$$\text{Difference in molecular orientation angle} = (\text{the minimum negative molecular orientation angle}) - (\text{the maximum negative molecular orientation angle}) \quad (5)$$

$$\text{Difference in molecular orientation angle} = 0 - (\text{the minimum negative molecular orientation angle}) \quad (6)$$

$$\text{Difference in molecular orientation angle} = (\text{the maximum positive molecular orientation angle}) \quad (7)$$

The difference between the maximum and the minimum of the molecular orientation angle in the present invention means a value calculated from any of the above equations using values among the molecular orientation angles at both end portions of a polyimide film and the molecular orientation angle at the central portion thereof.

The direction of the molecular orientation angle may be any direction as long as the difference in the molecular orientation angle is 40° or less. Preferably, the difference in the molecular orientation angle is 30° or less. When the difference between the maximum and the minimum of the molecular orientation angle is 40° or less, the variation in the amount of dimensional change can be reduced across the entire width of the film, thus being preferable.

Furthermore, in the present invention, the variation in the molecular orientation angle is specified. Namely, the molecular orientation angle is specified so as to be within 0±20° across the entire width of the polyimide film. When the film-transferring direction (MD direction) of the polyimide film is defined as a reference (0°) (10 in FIG. 3), the molecular orientation angle of the polyimide film is preferably within 0±20° across the entire width. The state that the molecular orientation angle in the present invention is within 0±20° can be described with reference to a drawing, i.e., FIG. 3, showing the relationship between the film-transferring direction (14 in FIG. 3) and the molecular orientation angle. The molecular orientation angle of 0° of the polyimide film means that the direction of the molecular orientation axis is parallel (10 in FIG. 3) to the MD direction. The molecular orientation angle of 20° represents the case where the angle is tilted in the

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counterclockwise direction from the MD direction (the angle shown by 11 in FIG. 3 being 20°). On the other hand, the molecular orientation angle of -20° represents the case where the angle is tilted in the clockwise direction from the MD direction (the angle shown by 12 in FIG. 3 being -20°). That is, the molecular orientation angle of 0±20°, which is preferred in the present invention, means that the molecular orientation angle is controlled so as to be within 20° in the left and right directions with respect to the MD direction.

An example of a method of producing a metal-clad laminate using a polyimide film as a base film is a method of applying an adhesive on the polyimide film, and then performing a thermocompression bonding with a metal foil (hot lamination method). In this method, during thermocompression bonding, the polyimide film is stretched with a thermocompression bonding apparatus in the MD direction of the film and is shrunk in the TD direction. When the molecular orientation axis is controlled to within 0±20°, the polyimide film is uniformly stretched in the MD direction across the entire width of the film. For example, in the case of a film having a width of 250 mm or more, uniform tension is applied across the entire width of the polyimide film along the MD direction. Consequently, when the polyimide film is stretched under heating, a stretching at one side of the film and curling of the film, which are caused by a difference in the elongation ratio between both end portions of the film, can also be suppressed. Accordingly, by controlling the molecular orientation angle as described above, in particular, when the hot lamination method is used, the rate of dimensional change can be decreased, and the rate of dimensional change can be stabilized across the entire width.

<Tear Propagation Resistance c in a Direction of Molecular Orientation Axis, Tear Propagation Resistance d in a Direction Perpendicular to Molecular Orientation Axis, and Tear Propagation Resistance Ratio d/c>

According to another embodiment of the polyimide film of the present invention, in a polyimide film produced by a continuous process, when the tear propagation resistance c in a direction of the molecular orientation axis and the tear propagation resistance d in a direction perpendicular to the molecular orientation axis are measured, the tear propagation resistance ratio d/c is in the range of 1.01 to 1.20, and more preferably in the range of 1.01 to 1.15 across the entire width of the polyimide film.

The tear propagation resistance c in a direction of the molecular orientation axis and the tear propagation resistance d in a direction perpendicular to the molecular orientation axis of the polyimide film in the present invention can be measured by the same procedures as those of the coefficient of linear expansion ratio A and the difference A_{DIFF} in coefficient of linear expansion ratio. Namely, measurement samples (40 mm×40 mm) are prepared from both end portions and the central portion of the width direction of the polyimide film, and the molecular orientation axes of the measurement samples are measured to determine the molecular orientation axes. Subsequently, as shown in FIG. 4, each measurement sample is respectively cut out (21 and 22 in FIG. 4) in a direction of the molecular orientation axis (20 in FIG. 4) and in a direction perpendicular to the molecular orientation axis (23 in FIG. 4). The tear propagation resistances of the cut out test pieces (10 mm×20 mm) are then measured to determine the above values. The tear propagation resistance is measured in accordance with American Society for Testing and Materials (ASTM) D1938 using the cut out test piece.

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In the present invention, in order to reduce the rate of dimensional change, the tear propagation resistance ratio calculated with the following equation (8) using the tear propagation resistance c in a direction of the molecular orientation axis and the tear propagation resistance d in a direction perpendicular to the molecular orientation axis is preferably in the range of 1.01 to 1.20, and more preferably in the range of 1.01 to 1.15.

$$\text{Tear propagation resistance ratio} = d/c \quad (8)$$

By controlling the tear propagation resistance ratio of the polyimide film to be within the above range, the rate of dimensional change of the polyimide film can be suppressed to a low value and the rate of dimensional change can be stabilized across the entire width of the film, thus being preferable.

Furthermore, in the present invention, from the viewpoint that not only the rate of dimensional change but also the variation in the physical property value (rate of dimensional change) in the width direction of the film can be reduced, the difference between the maximum and the minimum of the tear propagation resistance ratio is preferably 0.10 or less. In the phrase "the difference between the maximum and the minimum in the present invention is 0.10 or less", the difference means a value obtained by calculating the difference between the maximum and the minimum among the tear propagation resistance ratios at both end portions of the polyimide film and the tear propagation resistance ratio at the central portion thereof by the following equation (9).

$$\text{Difference between the maximum and the minimum of tear propagation resistance ratio} = \frac{\text{maximum tear propagation resistance ratio} - \text{minimum tear propagation resistance ratio}}{\text{maximum tear propagation resistance ratio}} \quad (9)$$

First, regarding the difference between the maximum and the minimum of the molecular orientation angle (for convenience, referred to as "difference in molecular orientation angle"), the upper limit of the difference in molecular orientation angle is 40° or less and more preferably 30° or less. In the case where the upper limit of the difference in molecular orientation angle is within the above range, when an FPC is formed with a metal layer, the variation in the rate of dimensional change in a base film including the polyimide can be reduced across the entire width, thus being preferable. In this case, the direction of the molecular orientation angle is not particularly limited, and may be any direction.

(II) Method of Producing a Polyimide Film of the Present Invention

The method of producing a polyimide film of the present invention is not particularly limited. The type of the polyimide resin is also not particularly limited. However, a method of changing the production conditions of the film can be used as means for obtaining a polyimide film wherein the coefficient of linear expansion ratio A represented by equation (1) is in the range of 1.01 to 3.00 across the entire width of the film, or a polyimide film of another embodiment of the present invention wherein when the tear propagation resistance c in a direction of the molecular orientation axis and the tear propagation resistance d in a direction perpendicular to the molecular orientation axis are measured, the tear propagation resistance ratio d/c is in the range of 1.01 to 1.20. In order to obtain a desired polyimide film, for example, a production method including

- (A) a step of preparing a polyamic acid by polymerization,
- (B) a step of casting or applying a composition containing the polyamic acid and an organic solvent on a support, and then forming a gel film,

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- (C) a step of peeling off the gel film and fixing both ends of the gel film, and
- (D) a step of transferring the film in a heating furnace with both ends of the film being fixed can be employed. The above polyimide film can be produced by appropriately selecting each of these conditions or adding other steps. Examples of the variable production conditions and production examples will be described below.

Step (A)

Step (A) is a process for polymerizing a polyamic acid. The polyamic acid is not particularly limited, but a polyamic acid solution prepared by allowing an acid dianhydride to react with a substantially equimolar amount of diamine in an organic solvent may be used.

Any known polymerization method can be used. Examples of particularly preferable polymerization method include the following methods:

- 1) A polymerization method in which an aromatic diamine is dissolved in a polar organic solvent, and is then allowed to react with a substantially equimolar amount of an aromatic tetracarboxylic dianhydride.
- 2) A polymerization method in which an aromatic tetracarboxylic dianhydride is allowed to react with fewer moles of an aromatic diamine compound in a polar organic solvent to prepare a prepolymer having acid anhydride groups at both terminals, and the aromatic diamine compound is then added so that the amount of the aromatic tetracarboxylic dianhydride and that of the aromatic diamine compound are substantially equimolar in the whole process.
- 3) A polymerization method in which an aromatic tetracarboxylic dianhydride is allowed to react with excessive moles of an aromatic diamine compound in a polar organic solvent to prepare a prepolymer having amino groups at both terminals, the aromatic diamine compound is further added to the prepolymer, and the aromatic tetracarboxylic dianhydride is then added so that the amount of the aromatic tetracarboxylic dianhydride and that of the aromatic diamine compound are substantially equimolar in the whole process.
- 4) A polymerization method in which an aromatic tetracarboxylic dianhydride is dissolved and/or dispersed in a polar organic solvent and substantially equimolar amount of an aromatic diamine compound is then added.
- 5) A polymerization method in which a mixture of substantially equimolar amounts of an aromatic tetracarboxylic dianhydride and an aromatic diamine is allowed to react in a polar organic solvent.

Examples of the organic solvent used in the preparation of the polyamic acid by polymerization include aprotic solvents such as ureas, e.g., tetramethylurea and N,N-dimethylethylurea; sulfoxides or sulfones, e.g., dimethyl sulfoxide, diphenylsulfone, and tetramethylsulfone; amides, e.g., N,N-dimethylacetamide (abbreviated as DMAc), N,N-dimethylformamide (abbreviated as DMF), N-methyl-2-pyrrolidone (abbreviated as NMP), γ -butyrolactone, and hexamethylphosphoric triamide; aprotic solvents, e.g., phosphorylamides; alkyl halides such as chloroform and methyl-ene chloride; aromatic hydrocarbons such as benzene and toluene; phenols such as phenol and cresol; and ethers such as dimethyl ether, diethyl ether, and p-cresol methyl ether. These solvents are generally used alone, but two or more solvents may be used in appropriate combinations properly. Among them, amides such as DMF, DMAc, and NMP are preferably used as the solvent in view of high solubility of polymers.

Regarding the weight percent of the solid content of the polyamic acid in the polyamic acid solution, in view of handling, 5 to 40 weight percent, preferably 10 to 30 weight

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percent, and more preferably 13 to 25 weight percent of the polyamic acid is dissolved in an organic solvent. In view of the physical properties of the film, the average molecular weight of the polyamic acid is 10,000 or more in terms of polyethylene glycol (PEG) by gel permeation chromatography (GPC).

The viscosity of the polyamic acid solution is measured with a B-type viscometer including a rotor No. 7 at a rotational speed of 4 rpm after the polyamic acid solution is kept for one hour in a water bath kept at 23° C. In view of easy handling in the production of a formed film, the viscosity is preferably in the range of 50 to 1,000 Pa·s, more preferably 100 to 500 Pa·s, and most preferably 200 to 350 Pa·s.

Examples of the acid dianhydride suitably used in the production of the polyamic acid solution of the present invention include acid ester anhydrides such as p-phenylene bis(trimellitic acid monoester anhydride), p-methylphenylene bis(trimellitic acid monoester anhydride), p-(2,3-dimethylphenylene) bis(trimellitic acid monoester anhydride), 4,4'-biphenylene bis(trimellitic acid monoester anhydride), 1,4-naphthalene bis(trimellitic acid monoester anhydride), 2,6-naphthalene bis(trimellitic acid monoester anhydride), and 2,2-bis(4-hydroxyphenyl)propanedibenzoate-3,3',4,4'-tetracarboxylic dianhydride; and dianhydrides such as ethylene-tetracarboxylic dianhydride, 1,2,3,4-butanetetracarboxylic dianhydride, cyclopentanetetracarboxylic dianhydride, pyromellitic dianhydride, 1,2,3,4-benzenetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,2',3,3'-benzophenonetetracarboxylic dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, bis(3,4-dicarboxyphenyl)ether dianhydride, bis(2,3-dicarboxyphenyl)ether dianhydride, bis(2,3-dicarboxyphenyl)sulfone dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 2,3,6,7-anthracenetetracarboxylic dianhydride, 1,2,7,8-phenanthrenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, 4,4'-(p-phenylenedioxy)diphthalic dianhydride, 4,4'-(m-phenylenedioxy)diphthalic dianhydride, and 2,2-bis[(2,3-dicarboxyphenoxy)phenyl]propane dianhydride. These may be used alone or in combinations of two or more.

Among them, at least one acid dianhydride selected from pyromellitic dianhydride, 1,2,3,4-benzenetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,2',3,3'-benzophenonetetracarboxylic dianhydride, and p-phenylenebis(trimellitic acid monoester anhydride) is preferably used because heat resistance is imparted to the polyimide film, and the elastic modulus of the film is improved, thereby easily controlling the orientation angle of the polyimide film.

Furthermore, the use of the above acid dianhydride is preferred because the average coefficient of linear expansion can be controlled to a preferable range.

When the elastic modulus of the polyimide film is improved, a volumetric shrinkage during volatilization of residual volatile components in the film generates a shrinkage stress in the plane of the film. The molecular orientation in the plane is accelerated by the shrinkage stress. As a result, the molecular orientation of the polyimide film proceeds. In addition, when the in-plane orientation proceeds, the average

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coefficient of linear expansion of the polyimide film can be controlled to be a low value. Thus, the average coefficient of linear expansion can be controlled to the preferable range in the present invention.

Examples of the amine compounds include p-phenylenediamine, m-phenylenediamine, o-phenylenediamine, 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl sulfide, 3,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfide, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminobenzophenone, 3,4'-diaminobenzophenone, 4,4'-diaminobenzophenone, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 2,2-bis(4-aminophenyl)propane, 2,2-bis(3-aminophenyl)propane, 2-(3-aminophenyl)-2-(4-aminophenyl)propane, 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane, 2,2-bis(3-aminophenyl)-1,1,1,3,3,3-hexafluoropropane, 2-(3-aminophenyl)-2-(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(3-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminobenzoyl)benzene, 1,4-bis(3-aminobenzoyl)benzene, 1,3-bis(4-aminobenzoyl)benzene, 1,4-bis(4-aminobenzoyl)benzene, 3,3'-diamino-4-phenoxybenzophenone, 4,4'-diamino-5-phenoxybenzophenone, 3,4'-diamino-4-phenoxybenzophenone, 3,4'-diamino-5-phenoxybenzophenone, 4,4'-bis(4-aminophenoxy)biphenyl, 3,3'-bis(4-aminophenoxy)biphenyl, 3,4'-bis(3-aminophenoxy)biphenyl, bis[4-(4-aminophenoxy)phenyl]ketone, bis[4-(3-aminophenoxy)phenyl]ketone, bis[3-(4-aminophenoxy)phenyl]ketone, bis[3-(3-aminophenoxy)phenyl]ketone, 3,3'-diamino-4,4'-diphenoxydibenzophenone, 4,4'-diamino-5,5'-diphenoxydibenzophenone, 3,4'-diamino-4,5'-diphenoxydibenzophenone, bis[4-(4-aminophenoxy)phenyl]sulfide, bis[3-(4-aminophenoxy)phenyl]sulfide, bis[4-(3-aminophenoxy)phenyl]sulfide, bis[3-(4-aminophenoxy)phenyl]sulfide, bis[3-(3-aminophenoxy)phenyl]sulfide, bis[3-(4-aminophenoxy)phenyl]sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, bis[3-(3-aminophenoxy)phenyl]sulfone, bis[4-(3-aminophenoxy)phenyl]sulfone, bis[4-(3-aminophenoxy)phenyl]ether, bis[4-(4-aminophenoxy)phenyl]ether, bis[3-(3-aminophenoxy)phenyl]ether, bis[4-(3-aminophenoxy)phenyl]methane, bis[4-(4-aminophenoxy)phenyl]methane, bis[3-(3-aminophenoxy)phenyl]methane, bis[3-(4-aminophenoxy)phenyl]methane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[3-(3-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 2,2-bis[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 2,2-bis[3-(3-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 2,2-bis[3-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 1,4-bis[4-(3-aminophenoxy)benzoyl]benzene, 1,3-bis[4-(3-aminophenoxy)benzoyl]benzene, 1,3-bis(3-amino-4-phenoxybenzoyl)benzene, 1,4-bis(3-amino-4-phenoxybenzoyl)benzene, 1,3-bis(4-amino-5-phenoxybenzoyl)benzene, 1,3-bis(4-amino-5-biphenoxybenzoyl)benzene, 1,4-bis(4-amino-5-biphenoxybenzoyl)benzene, 1,3-bis(3-amino-4-biphenoxybenzoyl)benzene, 1,4-bis(3-amino-4-biphenoxybenzoyl)benzene, 1,4-bis[4-(4-aminophenoxy)- α , α -dimethylbenzyl]benzene, 1,3-bis[4-(4-aminophenoxy)- α , α -dimethylbenzyl]benzene, 1,3-bis[4-(4-amino-6-trifluoromethylphenoxy)- α , α -dimethylbenzyl]benzene, 1,3-bis[4-(4-amino-6-fluoromethylphenoxy)- α , α -dimethylbenzyl]benzene, 1,3-bis(4-(4-amino-6-methylphenoxy)- α , α -

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dimethylbenzyl]benzene, 1,3-bis[4-(4-amino-6-cyanophenoxy)- α,α -dimethylbenzyl]benzene, and diaminopolysiloxane. These may be used alone or in combinations of two or more.

Among them, at least one compound selected from p-phenylenediamine, m-phenylenediamine, 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, and 2,2-bis[4-(4-aminophenoxy)phenyl]propane is preferably used from the standpoint that heat resistance of the polyimide film can be improved and the rigidity can be imparted to the film. Furthermore, p-phenylenediamine and/or 3,4'-diaminodiphenyl ether is preferably combined as an essential component because the elastic modulus of the polyimide film is improved, thereby easily controlling the orientation angle of the polyimide film. In addition, since the in-plane orientation proceeds, the average coefficient of linear expansion of the polyimide film can be controlled to be a low value. Thus, the average coefficient of linear expansion can be controlled to the preferable range in the present invention.

In the present invention, a high elastic modulus of the polyimide film is preferred from the viewpoint that the molecular orientation angle can be easily controlled to a preferable range. The elastic modulus was calculated as follows. The tensile moduli of the MD direction and the TD direction were measured using a sample prepared from the central portion (5 in FIG. 1) of the polyimide film. The elastic modulus was calculated using an equation:

$$\text{elastic modulus} = \{\text{tensile modulus in the MD direction} + \text{tensile modulus in the TD direction}\} / 2.$$

In view of the control of the orientation angle, the elastic modulus is preferably 4.2 GPa or more. The upper limit thereof is preferably 10.0 GPa or less because the flexibility during handling is not satisfactory.

Examples of particularly preferred polyimide film include:

1. A polyimide film prepared using four monomers including p-phenylenediamine, 4,4'-diaminodiphenyl ether, pyromellitic dianhydride, and p-phenylenebis(trimellitic acid monoester anhydride);

2. A polyimide film prepared using p-phenylenediamine, 4,4'-diaminodiphenyl ether, pyromellitic dianhydride, and 3,3',4,4'-biphenyltetracarboxylic dianhydride;

3. A polyimide film prepared using p-phenylenediamine, 4,4'-diaminodiphenyl ether, pyromellitic dianhydride, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride;

4. A polyimide film prepared using p-phenylenediamine, 4,4'-diaminodiphenyl ether, pyromellitic dianhydride, p-phenylenebis(trimellitic acid monoester anhydride), and 3,3',4,4'-biphenyltetracarboxylic dianhydride;

5. A polyimide film prepared using p-phenylenediamine, 4,4'-diaminodiphenyl ether, and 3,3',4,4'-biphenyltetracarboxylic dianhydride;

6. A polyimide film prepared using 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, and pyromellitic dianhydride;

7. A polyimide film prepared using p-phenylenediamine, 4,4'-diaminodiphenyl ether, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, pyromellitic dianhydride, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride; and

8. A polyimide film prepared using p-phenylenediamine and 3,3',4,4'-biphenyltetracarboxylic dianhydride. These polyimide films are advantageous in that the orientation of the film can be easily controlled and that the coefficient of linear expansion thereof can be controlled to be a low value, and thus are suitably used.

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Step (B)

In step (B), a composition (also referred as a polyamic acid solution) containing the polyamic acid and an organic solvent is cast or applied on a support to form a gel film. The composition used in step (B) may contain another component such as a reagent that can react with the polyamic acid.

The viscosity of the polyamic acid solution is measured with a B-type viscometer with a rotor No. 7 at a rotational speed of 4 rpm after the polyamic acid solution is kept for one hour in a water bath kept at 23° C. In view of easy handling in the production of a formed film, the viscosity is preferably in the range of 50 to 1,000 Pa·s, more preferably 100 to 500 Pa·s, and most preferably 200 to 350 Pa·s.

The solid content of the polyamic acid in the polyamic acid solution used in step (B) is in the range of 5 to 40 weight percent, preferably 10 to 30 weight percent, and more preferably 13 to 25 weight percent. In this range, the polyamic acid solution tends to be easily handled in the production of a formed film.

The viscosity and concentration of the polyamic acid solution can be controlled by, according to need, adding an organic solvent such as the polymerization solvent for polyamic acid described in step (A).

The polyimide film can be produced from the polyamic acid solution by a known method. The method includes a thermal imidization method and a chemical imidization method. In the thermal imidization method, imidization is accelerated by only heating. The heating conditions can be changed according to the type of the polyamic acid used, the thickness of the film, and the like. Furthermore, imidization is preferably performed using a polyamic acid solution containing a releasing agent, a thermal imidization catalyst, and the like, according to need. In the chemical imidization method, the polyamic acid solution is treated with an imidization catalyst and a dehydrating agent. Examples of the dehydrating agent include aliphatic acid anhydrides such as acetic anhydride, and aromatic acid anhydrides such as benzoic anhydride. Examples of the imidization catalyst include aliphatic tertiary amines such as triethylamine; aromatic tertiary amines such as dimethylaniline; and heterocyclic tertiary amines such as pyridine, picoline, and isoquinoline.

The amount of the imidization catalyst used is not particularly limited. However, the molar ratio of imidization catalyst/amido group in polyamic acid is preferably in the range of 10 to 0.01 and more preferably in the range of 5 to 0.5.

When the dehydrating agent and the imidization catalyst are combined, preferably, the molar ratio of dehydrating agent/amido group in polyamic acid is in the range of 10 to 0.01, and the molar ratio of imidization catalyst/amido group in polyamic acid is in the range of 10 to 0.01. More preferably, the molar ratio of dehydrating agent/amido group in polyamic acid is in the range of 5 to 0.5, and the molar ratio of imidization catalyst/amido group in polyamic acid is in the range of 5 to 0.5. In this case, a reaction retardant such as acetylacetone may be combined. The ratios of the dehydrating agent and the imidization catalyst to the polyamic acid may be determined by the time (pot life) required for the mixing of the polyamic acid and the dehydrating agent/catalyst mixture at 0° C. to the start of an increase in the viscosity. The pot life is generally in the range of 0.1 to 120 minutes and preferably in the range of 1 to 60 minutes.

Additives such as a thermal stabilizer, an antioxidant, an ultraviolet absorber, an antistatic agent, a flame retardant, a pigment, a dye, a fatty acid ester, an organic lubricant (e.g. wax) may also be added. Furthermore, in order to impart lubricity, abrasion resistance, scratch resistance, and the like to the film surface, inorganic particles of clay, mica, titanium

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oxide, calcium carbonate, kaolin, talc, wet- or dry-process silica, colloidal silica, calcium phosphate, calcium hydrogen phosphate, barium sulfate, alumina, zirconia, or the like, or organic particles containing acrylic acids, styrene, or the like as the component may be added.

When the polyamic acid solution containing the imidization catalyst, the dehydrating agent, the additives, and the like is prepared, a step of removing insoluble raw materials and foreign substances through a filter or the like is preferably performed before mixing these components in order to reduce the foreign substances and defects in the film. The opening of the filter is $\frac{1}{2}$, preferably $\frac{1}{5}$, and more preferably $\frac{1}{10}$ of the thickness of the film produced.

The polyamic acid solution prepared as described above is continuously cast or applied on a support, and is then dried to form a gel film. As the support, any support can be used as long as the support is not dissolved by the solution resin and can resist heating that is necessary for removing the organic solvent from the polyimide solution. In particular, an endless belt or a metal drum, which is produced by joining metal plates together, is preferred for drying the coated solution. The material of the endless belt or the metal drum is preferably a metal, and in particular, a SUS (stainless steel) material is preferably used. The surface of the support is preferably plated with a metal such as chromium, titanium, nickel, or cobalt because the adhesiveness of the solvent to the surface is improved or a dry organic insulating film can be easily peeled off. The endless belt or the metal drum preferably has a smooth surface. Alternatively, innumerable irregularities may be formed on the endless belt or the metal drum. The irregularities processed on the endless belt or the metal drum preferably have a diameter of 0.1 to 100 μm and a depth of 0.1 to 100 μm . By forming the irregularities on the metal surface, fine projections can be formed on the surface of the organic insulating film. Consequently, the projections can suppress the occurrence of flaws caused by friction between films or can improve slippage between the films.

The gel film of the present invention will be described. The term "gel film" means a state in which a part of the organic solvent or reaction products (referred to as "residual component") remain in the film after the organic solvent solution containing the polyamic acid and the organic solvent is dried by heating. In the process of producing the polyimide film, the organic solvent dissolving the polyamic acid solution, the imidization catalyst, the dehydrating agent, and the reaction products (hygroscopic component of the dehydrating agent and water) remain as the residual component in the gel film. The ratio of the residual component in the gel film is calculated using the following equation (10):

$$c = b/ax100 \quad (10)$$

wherein a represents the weight (g) of completely dry polyimide, b represents the weight (g) of the residual component contained in the gel film, and c represents the ratio of the residual component. The ratio of the residual component is preferably 500% or less, more preferably in the range of 25% to 200%, and particularly preferably in the range of 30% to 150%.

When the ratio of the residual component is more than 500%, handleability is not satisfactory, and the film is significantly shrinks during removal of the solvent. Consequently, undesirably, it is difficult to stabilize the orientation angle or the physical property values (rate of dimensional change) across the entire width of the film. The ratio of the residual component is preferably 25% or more because the orientation angle of the polyimide film is easily aligned in the MD direc-

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tion (0°), and the physical property values of the film in the width direction is easily stabilized.

The weight a of completely dry polyimide and the weight b of the residual component are calculated as follows: The weight d of a gel film of 100 mm \times 100 mm is measured. The gel film is then dried in an oven at 300 $^\circ$ C. for 20 minutes, and cooled to room temperature. The weight of the dry gel film is measured as the weight a of completely dry polyimide. The weight b of the residual component is calculated from the weight d of the gel film and the weight a of completely dry polyimide according to the equation of $b = d - a$.

In the step of producing the gel film, the temperature, wind speed, and exhaust speed during drying by heating on the support are preferably determined so that the ratio of the residual component is in the above range. In particular, in the production process of the polyimide film, the organic solvent solution containing the polymer and the organic solvent is preferably dried by heating at a temperature in the range of 50 $^\circ$ C. to 200 $^\circ$ C. and particularly preferably 50 $^\circ$ C. to 180 $^\circ$ C. The drying time is preferably in the range of 1 to 300 minutes, and the gel film is preferably dried under a multi-stage temperature control system.

Step (C)

In step (C), the gel film is peeled off from the support and the both ends of the gel film are continuously fixed. In the step of fixing the ends of the gel film in the present invention, ends of the gel film are gripped using gripping devices that are generally used in a film-producing apparatus, such as pin seats, clips, or the like. For example, the end gripping positions in the present invention are positions 37 shown in FIG. 5 at which gripping of the film ends with end gripping devices (pin seats or clips) is started in a film transfer apparatus 31 shown in FIG. 5.

As a method of fixing the gel film so that substantially no tension is applied in the TD direction during at least a part of step (D) described below, when the ends of the gel film are fixed in step (C), the gel film may be fixed so that substantially no tension is applied in the TD direction. That is, the film is fixed so that substantially no tension is applied in the TD direction, and is then transferred to step (D) as it is. Specifically, the ends of the film are fixed so that the film sags.

Step (D)

In step (D), the film is transferred in a heating furnace with both ends of the film being fixed. In the present invention, from the standpoint that the polyimide film intended in the present invention is produced, it is important that the film is transferred while being fixed so that substantially no tension is applied in the film width direction (TD direction) during at least a part (referred to as "step (D-1)") of step (D).

The phrase "substantially no tension is applied in the TD direction" means that tensile tension due to mechanical handling is not applied in the TD direction except for the tension due to the weight of the film itself. Substantially, this means that the width (39 in FIG. 6) of the film between both fixed ends is larger than the distance (38 in FIG. 6) between both fixed ends of the film. The film under such a condition is referred to as "a film on which substantially no tension is applied". This state will be described with reference to FIG. 6. The film is fixed by the gripping devices, and a length (38 shown in FIG. 6) in this state corresponds the distance between the ends of both end gripping devices. Tension is usually applied at both ends of the film, and, in this state, the distance 38 between both fixed ends is the same as the width 39 of the film between both fixed ends. In the present invention, as shown in FIG. 6, the distance 38 between both fixed ends is different from the width 39 of the film between both fixed ends, that is, the distance between both fixed ends is

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smaller than the width of the film. Specifically, the film is fixed so as to have a sag. In particular, from the standpoint that desirable characteristics of the present invention can easily exhibit, the film is preferably fixed so as to satisfy the following formula:

$$20.0 > (Y-X)/Y \times 100 > 0.00 \quad (11)$$

wherein X represents the distance 38 between both fixed ends, and Y represents the width 39 of the film between both fixed ends. When the ratio $(Y-X)/Y \times 100$ (may be referred to as "TD shrinkage ratio" for convenience) exceeds the above range, it is difficult to stably control the sag of the film, and the amount of sag may vary in the transfer direction. Furthermore, in some cases, the film may drop from the end gripping devices because of the sag of the film, and thus the film cannot be stably produced. The ratio is more preferably $15.0 \geq (Y-X)/Y \times 100 > 0.00$, and particularly preferably $10.0 \geq (Y-X)/Y \times 100 > 0.00$.

In the present invention, the film is preferably fixed so that substantially no tension is applied in the TD direction at the entrance of the heating furnace in step (D) from the standpoint that the film can be controlled so as to have the most desirable orientation state across the entire width of the film, thereby producing the polyimide film that exhibits the desirable characteristics in the present invention. In order that the film is transferred while being fixed so that substantially no tension is applied in the TD direction at the entrance of the heating furnace, the following methods can be employed. In step (C), both ends of the gel film are fixed so that substantially no tension is applied in the TD direction, the film is then transferred to step (D) as it is (first method). An operation (process shown in FIG. 5) of decreasing the distance between both fixed ends is performed after step (C), and the film is then transferred to step (D) (second method). In the first method, both ends of the gel film are preferably fixed so as to satisfy formula (11). In the second method, the distance between the fixed ends is preferably decreased so as to satisfy formula (11).

After the first or second method is performed and the gel film is then introduced into the heating furnace in step (D), the operation of decreasing the distance between both fixed ends may be performed (third method). In the third method, the operation of decreasing the distance between both fixed ends is preferably performed in the temperature range of 300° C. or lower, more preferably 250° C. or lower, and particularly preferably 200° C. or lower. When the operation in the third method is performed in the temperature range over 300° C., it may be difficult to control the difference between the maximum A_{MAX} and the minimum A_{MIN} of the coefficient of linear expansion ratio A to a low value or control the difference between the maximum and the minimum of the tear propagation resistance ratio to a low value across the entire width of the film.

In the present invention, as described above, it is important that the gel film undergoes a state in which substantially no tension is applied in the TD direction immediately before a temperature is applied to the gel film.

In step (D), since the film is dried and imidization further proceeds, the film is shrunk to some extent. Therefore, when the film is transferred while being fixed so that substantially no tension is applied in the TD direction at the entrance of the heating furnace, the width of the film is decreased because of thermal shrinkage of the film. Consequently, the width of the film between both fixed ends becomes the same as the distance between both fixed ends, and thus the film without wrinkles can be produced.

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In the present invention, step (D) may include a step (step (D-2)) of stretching the film in the TD direction. When step (D) further includes step (D-2), it is possible to control the coefficient of linear expansion ratio and the tear propagation resistance ratio of the film.

Specifically, in order to stabilize the coefficient of linear expansion ratio and the tear propagation resistance ratio of the polyimide film across the entire width and to produce the polyimide film having low values of the coefficient of linear expansion ratio and the tear propagation resistance ratio, the production method including step (D-2) may be employed.

In step (D-2) in the present invention, the film is stretched in the TD direction in the heating furnace after step (D-1). In step (D-1), the film is transferred while being fixed so that no tension is applied in the film width direction (TD direction). In this step, when the film is heated in the heating furnace, the film is shrunk to some extent. After the sag of the film is removed by shrinking, the film is stretched in the TD direction. The amount of stretching preferably satisfies the following formula:

$$40.0 \geq (W-Z)/Z \times 100 > 0.00 \quad (12)$$

wherein Z represents the width (for example, 41 in FIG. 5) between both fixed ends in the TD direction before stretching, and W represents the width (for example, 42 in FIG. 5) between both fixed ends after the film is stretched in the TD direction in the furnace. When the ratio $(W-Z)/Z \times 100$ (may be referred to as "TD expansion ratio" for convenience) exceeds the above range, it may be difficult to control the coefficient of linear expansion ratio and the tear propagation resistance ratio of the film to low values in a uniform level across the entire width. The ratio is more preferably $30.0 \geq (W-Z)/Z \times 100 > 0.00$, and particularly preferably $20.0 \geq (W-Z)/Z \times 100 > 0.00$. In step (D-2), the film may be stretched in the TD direction while the width of the film between the gripping positions is gradually increased. If necessary, shrinking may be again performed after step (D-2), and the width of the film may be further increased. Preferably, the TD shrinkage ratio and the TD expansion ratio are appropriately selected.

In order to control the coefficient of linear expansion ratio and the tear propagation resistance ratio of the film to desired ranges, the relationship between the TD shrinkage ratio and the TD expansion ratio preferably satisfies the following formula:

$$10.0 \geq \text{TD shrinkage ratio} - \text{TD expansion ratio} \geq -10.0 \quad (13)$$

More preferably, $8.0 \geq \text{TD shrinkage ratio} - \text{TD expansion ratio} \geq -8.0$, and particularly preferably $5.0 \geq \text{TD shrinkage ratio} - \text{TD expansion ratio} \geq -5.0$.

The temperature in step (D-2) is preferably in the range of 300° C. to 500° C. and particularly preferably in the range of 350° C. to 480° C. because the elastic modulus of the polyimide film is decreased, thereby easily stretching the film. At the above temperature, the film may be overstretched because of softening of the film. In such a case, the temperature is preferably appropriately set outside the above range.

Furthermore, in step (D-2), the coefficient of linear expansion ratio and the tear propagation resistance ratio of the film can be controlled to low values by adjusting the TD expansion ratio. That is, the coefficient of linear expansion ratio and the tear propagation resistance ratio of the film can be freely controlled by stretching the film in step (D-2).

In the present invention, shrinkage in step (D-1), stretching in step (D-2), film tension in the MD direction during transfer, the weight of the residual component of the gel film, and the heating temperature may be appropriately adjusted to pro-

duce the film having desired coefficient of linear expansion ratio and the tear propagation resistance ratio. The heating temperature and the heating time of the film are completely different depending on imidization method including chemical imidization or thermal imidization. However, even in thermal imidization, the intended film can be produced by controlling conditions according to the method of the present invention.

The heating furnace that is preferably used in the present invention includes an air-heating furnace in which hot air at 60° C. or higher is blasted on the entire film from the lower or upper surface or both surfaces of the film, and a far-infrared furnace including a far-infrared generator for baking the film by irradiating the film with far-infrared rays. In the heating step, the film is preferably baked by increasing the temperature stepwise. For this purpose, a heating furnace for increasing the temperature stepwise is preferably used in which a plurality of air-heating furnaces, far-infrared furnaces, or air-heating furnaces and far-infrared furnaces are connected to perform baking.

In the process of producing the polyimide film of the present invention, when the gel film is gripped and transferred in the furnace in the baking step, the first heating temperature is preferably 300° C. or lower, more preferably in the range of 60° C. to 250° C., and particularly preferably in the range of 100° C. to 200° C. in order to control the difference between the maximum A_{MAX} and the minimum A_{MIN} of the coefficient of linear expansion ratio A to a low value or control the difference between the maximum and the minimum of the tear propagation resistance ratio to a low value across the entire width of the film. Specifically, the film is preferably transferred through two or more heating furnaces and the temperature of a first heating furnace (32 in FIG. 5) is preferably controlled to 300° C. or lower. When the furnaces are applied to the production of another polyimide film, the heating temperature is preferably determined in consideration of the type of the polyimide film and the evaporation temperature of the solvent used. In particular, preferably, the boiling point of the solvent contained in the gel film is measured, and the heating temperature is controlled to a temperature not more than 100° C. higher than the boiling point of the solvent.

In the production of the polyimide film, when the first heating temperature in the furnace in which the gel film is transferred is higher than 300° C., bowing phenomenon (a phenomenon in which a strong molecular orientation occurs at the ends of the film because the central portion of the film is transferred in the heating furnace earlier than the ends thereof because of the influence of shrinkage of the film) may occur, resulting in a difficulty of controlling the orientation angles at the ends of the film. Furthermore, it may be difficult to control the difference between the maximum A_{MAX} and the minimum A_{MIN} of the coefficient of linear expansion ratio A and the difference between the maximum and the minimum of the tear propagation resistance ratio to low values. In the baking of the polyimide film, the temperature of a second furnace 33 shown in FIG. 5 is preferably set in the range of 50° C. to 300° C. higher than the temperature of the first furnace 32 shown in FIG. 5 and particularly preferably in the range of 60° C. to 250° C. higher than the temperature of the first furnace 32 shown in FIG. 5 in view of control of the molecular orientation angle of the polyimide film. In the subsequent furnaces, baking is preferably performed at temperatures that are generally used in the production of polyimide films. However, when the temperature of the first furnace (32 in FIG. 5) is 60° C. or lower, the temperature of the next furnace (33 in FIG. 5) is preferably set in the range of 100° C. to 250° C. When the temperature of the first furnace (32 in

FIG. 5) is 60° C. or lower, the temperature of the second furnace is preferably set to the above value in order to control the difference between the maximum A_{MAX} and the minimum A_{MIN} of the coefficient of linear expansion ratio A to a low value or control the difference between the maximum and the minimum of the tear propagation resistance ratio to a low value across the entire width of the film. In the baking step, although the temperatures of the first furnace and the next furnace are set as described above, the other temperatures are preferably set to baking temperatures that are generally used in the production of polyimide films. In an example of a method, a polyimide film can be baked by increasing the temperature stepwise to 600° C. at the maximum, and then gradually cooled to room temperature. When the maximum baking temperature is low, imidization may not be completely performed. Therefore, sufficient baking is necessary.

When the gel film is transferred to the furnace, the tension applied to the gel film in the MD direction is calculated in terms of tension (load) applied per meter of the film. The tension is preferably in the range of 1 to 20 kg/m, more preferably in the range of 1 to 15 kg/m, and particularly preferably in the range of 1 to 10 kg/m. When the tension is less than 1 kg/m, it is difficult to stably transfer the film, and thus stable film production tends to become difficult while the film is gripped. When the tension applied to the film is more than 20 kg/m, in particular, it is difficult to control the orientation angles at the ends of the film, and in addition, the coefficient of linear expansion ratios and the tear propagation resistance ratios at the ends of the film are higher than those in the central portion. Consequently, it tends to become difficult to control the coefficient of linear expansion ratio and the tear propagation resistance ratio to uniform values across the entire width. Examples of a tension generator for applying tension to the gel film transferred to the furnace include a load roll for applying a load to the gel film, a roll for changing a load by adjusting the rotational speed of the roll, a nip roll for controlling tension by nipping the gel film between two rolls. The tension applied to the gel film can be adjusted by a method using the above tension generator.

Preferably, the tension applied to the film is appropriately adjusted in the above range depending on the thickness of the polyimide film. In view of formability of the polyimide film, the thickness of the film is preferably in the range of 1 to 200 μ m and particularly preferably in the range of 1 to 100 μ m. When the thickness of the film is more than 200 μ m, the shrinkage stress generated in the film may be increased, and thus it may be impossible to control the coefficient of linear expansion ratio and the tear propagation resistance ratio of the film, and the orientation angle thereof.

The polyimide film produced by the production method of the present invention may be subjected to any desired process such as heat treatment, forming, surface treatment, lamination, coating, printing, embossing, or etching according to need.

(III) Use of the Invention

The polyimide film produced by the above-described production method of the present invention can be used for any application. Examples of the application include applications to electric and electronic device substrates such as base films for FPCs, TAB tapes, and high-density recording media; applications to solar cell substrates; applications to magnetic recording media; and applications to electric insulation. In particular, the polyimide film can be preferably used as the base film for FPC. As described in section (I), in the polyimide film of the present invention, in particular, the rate of dimensional change across the entire width can be small, and the dimensional stability across the entire width can be satis-

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factory before and after etching in the production process of FPC. As a result, the polyimide film can be suitably used as the base film of FPC for high-density mounting.

The polyimide film of the present invention may be a single layer film composed of only the polyimide film, but the polyimide film may be also a laminate including another layer. Specifically, for example, another polymer layer may be applied or laminated on at least one surface of the polyimide film. Examples of the other resin layer to be laminated include, but are not particularly limited to, layers of thermoplastic polyimides, polyesters, polyolefins, polyamides, polyvinylidene chloride, acrylic polymers, and fluorocarbon polymers. These polymer layers may be laminated directly on the polyimide film or with an adhesive layer therebetween.

After a gel film is formed, for example, the laminate can be preferably produced by the following method: (1) a method of dipping the gel film in a solution (referred to as "another resin solution") prepared by dissolving another resin, and then drying the film in a tenter furnace by heating to produce a laminated film, (2) a method of applying another resin solution on a surface of the gel film using a coater, and then drying the film by heating to produce a laminated film, or (3) a method of spray-coating another resin solution on the gel film using a spray device, and then drying the film by heating to produce a laminated film. Alternatively, another resin solution may be again applied on a surface of the formed polyimide film, and then dried by heating to produce a laminated film. In this case, any one of the lamination methods (1) to (3) is preferably used as the application method. The laminate (or laminated film) in the present invention may be any laminate that includes at least one layer of the other resin.

Furthermore, examples of a method that is preferably used for producing a metal-clad laminate (laminate) in which a metal is laminated with the polyimide film include (1) a method of laminating an adhesive layer on at least one surface of the polyimide film, and then performing thermocompression bonding of a metal on the adhesive layer (preferably using, for example, a pressing method, a double belt method, or a hot roll method); (2) a method of laminating (vacuum laminating) a metal directly on at least one surface of the polyimide film in a vacuum apparatus; (3) a method of thickly laminating a metal layer on the metal-clad laminate, which is produced by the vacuum lamination in method (2), by metal plating or electroless plating; (4) a method of thinly laminating a metal by electroless plating; and (5) a method of thickly laminating a metal layer on the metal layer, which is thinly laminated by electroless plating in method (4), by metal plating or electroless plating.

The metal-clad laminate produced as described above is subjected to a wiring formation process for the metal layer (by, for example, a method of forming an etching mask on the surface, and then etching the metal layer) to form metal wiring on the base film including at least the polyimide film.

In method (1) among methods of (1) to (5) that can be preferably used in the present invention, examples of the adhesive that can be suitably used include, but are not particularly limited to, thermoplastic polyimide resin adhesives (adhesives containing at least a polyimide resin), acrylic adhesives (adhesives containing at least an acrylic resin), and epoxy adhesives (adhesives containing at least an epoxy resin). In production method (1), a metal foil of copper, aluminum, gold, silver, nickel, chromium, or an alloy thereof having a thickness of at least 0.1 μm is used as the metal. Furthermore, in the laminate having the adhesive layer, which is produced by production method (1), a protective material may be laminated for protecting the adhesive layer.

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Examples of a method that is preferably used for laminating in the vacuum apparatus in production method (2) include a heating evaporation method in which a metal is laminated by heating evaporation in a heating furnace, an electron beam method in which a metal is laminated by heating evaporation using an electron beam, and a sputtering method in which a metal is laminated by evaporation using plasma. The metal used in this method is not particularly limited, but copper, gold, silver, manganese, nickel, chromium, titanium, tin, cobalt, indium, molybdenum, or the like is preferably used. These metals may be used alone. Alternatively, a plurality of the types of the metals may be simultaneously evaporated to form a metal alloy on a surface of the polyimide film. Examples of such a method include a method of simultaneously laminating nickel and chromium to form a nickel/chromium alloy, and a method of simultaneously evaporating indium and tin in the presence oxygen to form an indium tin oxide (ITO) film.

Furthermore, in a method of electroless plating used in production method (4), a catalyst metal for electroless plating is laminated on a surface of the polyimide film, and the polyimide film is then immersed in a metal-containing bath for electroless plating to laminate the metal. The electroless plating method is not limited to the above method, and a method of laminating a metal by a known electroless plating technique can be preferably used.

In a method of electroplating in production methods (3) and (5), for example, the metal-clad polyimide film produced by production method (2) or (4) is immersed in a solution prepared by dissolving a metal to be plated, and a current is then supplied using the metal to be electroplated as a counter electrode to perform plating. The electroplating method is not limited to the above method, and a method of laminating a metal by a known electroplating technique can be preferably used.

In a method of thickly laminating the metal by electroless plating, for example, a film prepared by applying a catalyst for electroless plating on a surface of the metal-clad polyimide film produced by production method (2) or (4) is immersed in an electroless plating bath prepared by dissolving a desired metal to laminate the metal. The electroless plating method is not limited to the above method, and a method of laminating a metal by a known electroless plating technique can be preferably used.

A protective material for protecting the metal layer may be laminated on the metal-clad polyimide film produced by production methods (1) to (5).

As described above, the laminate of the present invention is not particularly limited as long as it includes the polyimide film of the present invention. Furthermore, although representative examples of the method of producing the metal laminate have been described in detail above, the present invention is not limited thereto. Accordingly, the present invention also includes a method of producing a metal laminate (for example, a metal-clad laminate for FPC, TAB, high-density recording media, magnetic recording media, or electrical and electronic devices) produced by using the polyimide film as a base film and the above flexible metal-clad laminate. The method of producing the FPC or the flexible metal-clad laminate is not limited to the above-described methods. Various known methods that can be used by those skilled in the art may be used to laminate the metal layer.

EXAMPLES

The present invention will now be specifically described on the basis of examples, but is not limited by these examples.

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Persons skilled in the art can make various changes, adjustments, and modifications without departing from the scope of the present invention. The coefficient of linear expansion ratio, the tear propagation resistance ratio, and the molecular orientation angle of the polyimide film of the present invention, the rate of dimensional change of the flexible metal-clad laminate, and the elastic modulus were measured and evaluated as described below.

[Coefficient of Linear Expansion Ratio]

As shown in FIG. 2, strip measurement samples **3** and **4** of a polyimide film **2** were respectively cut out along the direction of the molecular orientation axis (D_{AL} in the figure) and the perpendicular direction (D_{VE}). The coefficient of linear expansion a in the direction of the molecular orientation axis was measured using the measurement sample **3** cut out along the direction of the molecular orientation axis. The coefficient of linear expansion b in the perpendicular direction was measured using the measurement sample **4** cut out along the perpendicular direction. A thermomechanical analyzer (manufactured by Seiko Instruments Inc., trade name: TMA120C) was used as the measurement device. The samples were heated in the temperature range of 10° C. to 400° C. under a nitrogen stream at a heating rate of 10° C./min. The measured values in the temperature range of 100° C. to 200° C. were averaged.

The coefficient of linear expansion ratio A of the polyimide film **2** was calculated from the coefficients of linear expansion a and b in the respective directions using equation (1). Furthermore, the difference between the maximum A_{MAX} and the minimum A_{MIN} (difference A_{DIF} in coefficient of linear expansion ratio= $A_{MAX}-A_{MIN}$) was calculated from the calculated coefficient of linear expansion ratio A .

[Molecular Orientation Angle]

The molecular orientation angles at both end portions and at the central portion of the polyimide film were measured with a molecular orientation analyzer (manufactured by Oji Scientific Instruments, trade name: MOA 2012). Specifically, as shown in FIG. 3, it was confirmed whether the molecular orientation angle was within $\pm 20^\circ$ on the basis of the reference (0°) of the MD direction shown by **10** in FIG. 3, when the MD direction (**14** in FIG. 3, i.e., the transfer direction of the polyimide film) and the direction perpendicular to the MD direction (**15** in FIG. 3, i.e., the TD direction) were determined. Furthermore, the difference in molecular orientation angle was calculated from the difference between the maximum and the minimum of the calculated molecular orientation angles.

[Rate of Dimensional Change]

As shown in FIG. 7, in a rolled flexible metal-clad laminate **50**, the flexible metal-clad laminate **50** was pulled out and measurement samples **51**, **52**, and **53** each having desired dimensions were prepared from both end portions and the central portion of the laminate along the width direction. As shown in FIG. 8, the rates of dimensional change of the measurement samples **51** to **53** were measured (1) in the measurement direction along the MD direction (an arrow D_1 in the figure) shown by double-ended arrows D_{MD} in the figure, (2) in the direction along the TD direction (the direction perpendicular to the MD direction) shown by double-ended arrows D_{TD} in the figure, (3) in the direction (R direction) tilted by 45° rightward from the MD direction shown by a double-ended arrow D_R in the figure, and (4) in the direction (L direction) tilted by 45° (-45° when the rightward tilt is defined as being on the plus side) leftward from the MD direction shown by a double-ended arrow D_L in the figure.

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The dimensional change was measured according to the method specified in Japanese Industrial Standards (JIS) C6481. Specifically, holes **60** (see FIG. 8) for measurement were formed at four corners of each of the measurement samples **51** to **53**. The distances between the holes **60**, that is, the dimensions in the D_{MD} , D_{TD} , D_R , and D_L directions were measured. Next, the measurement samples **51** to **53** were etched to remove a metal foil, and were then left to stand in a thermostatic chamber at 20° C. and 60% R.H. for 24 hours.

Subsequently, the distances between the holes **60** were measured as before the etching. The rate of dimensional change before and after the etching was calculated using the following equation (14):

$$\text{Rate of dimensional change (\%)} = \{(M_2 - M_1) / M_1\} \times 100 \quad (14)$$

wherein M_1 is the measured distance between the holes before the removal of the metal foil and M_2 is the measured distance between the holes after the removal of the metal foil.

[Measurement of Tear Propagation Resistance and Tear Propagation Resistance Ratio]

Samples for measuring the molecular orientation angle described below were prepared from the both end portions and the central portion, and the molecular orientation angle was measured. The molecular orientation axis was determined from the measurement result of the molecular orientation angle. As shown in FIG. 4, from the above samples, test pieces (10 mm×20 mm) were respectively cut out in a direction of the molecular orientation axis and in a direction perpendicular to the molecular orientation axis. The measurement was performed in accordance with ASTM D1938 using the above test pieces.

[Measurement of Elastic Modulus]

Test pieces (15 mm×200 mm) were respectively cut out in the MD direction and the TD direction using the part **5** shown in FIG. 1. The measurement was performed in accordance with ASTM-D882 with a tensile testing machine manufactured by Shimadzu Corporation (Autograph S-100-C) using the test pieces.

Example 1

Production of Polyimide Film

To an organic solvent N,N-dimethylformamide (DMF) for polymerization, 50 mole percent of 4,4-diaminodiphenyl ether (ODA), 50 mole percent of p-phenylenediamine (p-PDA), 50 mole percent of p-phenylenebis(trimellitic acid monoester anhydride) (TMHQ), and 50 mole percent of pyromellitic dianhydride (PMDA) were added and polymerized under stirring to synthesize a polyamic acid solution. The synthesis was performed so that the solid content of the resulting polyamic acid solution was 15 weight percent.

To the polyamic acid solution, 2.0 equivalents of acetic anhydride and 1.0 equivalent of isoquinoline relative to the equivalent of the amic acid were added, and the solution was cast onto an endless belt so that the layer of the solution had a thickness of 20 μm at a width of 1,100 mm. The solution was dried with hot air in the temperature range of 100° C. to 150° C. for two minutes to prepare a self-supporting gel film (polyimide precursor film). The residual component ratio of the gel film was 54 weight percent. The gel film was peeled off from the endless belt, and both ends of the gel film in the width direction were fixed without a sag on pin seats that continuously transfer the film. The distance between the pin seats was 1,000 mm.

The gel film was baked stepwise in a first heating furnace (177° C.), a second heating furnace (300° C.), a third heating furnace (450° C.), and a fourth heating furnace (515° C.) to advance imidization, thereby obtaining a polyimide film. In this process, the gel film was transferred to the tenter furnace and in the tenter furnace while being shrunk and/or expanded in the TD direction so as to adjust the TD shrinkage ratio to 4.40 and the TD expansion ratio to 2.20. The step of decreasing the distance between both fixed ends so that substantially no tension was applied to the film in the TD direction was completed before the film was introduced into the furnace. The step of increasing the distance between both fixed ends was performed in the third heating furnace.

The conditions for producing the polyimide film are shown in Table 1.

The molecular orientation angles, the difference in molecular orientation angle, the coefficients of linear expansion, the coefficient of linear expansion ratios A , the difference A_{DIF} in coefficient of linear expansion ratio, the tear propagation resistances, the tear propagation resistance ratios, the difference between the maximum and the minimum of the tear propagation resistance ratio, and the angles of the molecular orientation axis of the prepared polyimide film were measured. The results are shown in Tables 2 and 3. In Table 2, rows corresponding to an end portion, the central portion, and another end portion are provided for each example (or comparative example) to show the results of the measurement samples 51, 52, and 53. As is apparent from the results shown in Tables 2 and 3, in the polyimide film, the coefficient of linear expansion ratio A was controlled in the range of 1.01 to 3.00, the difference A_{DIF} in coefficient of linear expansion ratio was controlled to 0.30 or less, the tear propagation resistance ratio was controlled in the range of 1.01 to 1.20, the difference between the maximum and the minimum of the tear propagation resistance ratio was controlled to 0.10 or less, and the angle of the molecular orientation axis was controlled to $0 \pm 20^\circ$ across the entire width of the film. Furthermore, the average coefficient of linear expansion C_{LE} was calculated using the following equation (2). In equation (2), as shown in FIG. 2, the coefficient of linear expansion in a direction of the molecular orientation axis (D_{AL} in the figure) at an end is defined as $C1_{AL}$, the coefficient of linear expansion in the perpendicular direction (D_{VE}) at the end is defined as $C1_{VE}$, the coefficient of linear expansion in the direction of the molecular orientation axis (D_{AL} in the figure) at the center is defined as $C0_{AL}$, the coefficient of linear expansion in the perpendicular direction (D_{VE}) at the center is defined as $C0_{VE}$, the coefficient of linear expansion in the direction of the molecular orientation axis (D_{AL} in the figure) at another other end is defined as $C2_{AL}$, and the coefficient of linear expansion in the perpendicular direction (D_{VE}) at the other end is defined as $C2_{VE}$.

$$C_{LE} = \frac{\{(C1_{AL} + C1_{VE})/2 + (C0_{AL} + C0_{VE})/2 + (C2_{AL} + C2_{VE})/2\}}{3} \quad (2)$$

The average coefficient of linear expansion C_{LE} calculated from the equation (2) was 12.8 ppm/ $^\circ$ C.

The polyimide film had an elastic modulus of 6.1 GPa.

<Synthesis of Thermoplastic Polyimide Precursor Used as Adhesive Layer>

To an organic solvent DMF for polymerization, 100 mole percent of bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS), 90 mole percent of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), and 10 mole percent of 3,3',4,4'-ethylene glycol benzoate tetracarboxylic dianhydride (TMEG) were added and polymerized under stirring to synthesize a

polyamic acid solution serving as the precursor of a thermoplastic polyimide. The synthesis was performed so that the solid content of the resulting polyamic acid solution was 20 weight percent.

<Production of Flexible Metal-Clad Laminate>

The polyimide film was preliminarily subjected to a surface plasma treatment by performing plasma discharge at an output of 280 W/m² in a mixed gas stream of Ar:He:N₂=8:2:0.2 (volume ratio) on the surface of the polyimide film. The above-described thermoplastic polyimide precursor was diluted with DMF to a solid content of 10 weight percent. Subsequently, the diluted thermoplastic polyimide precursor was applied on both surfaces of the polyimide film across the entire width so that the final thickness of the thermoplastic polyimide layer at one surface was 4 μ m, and the polyimide film was then heated at 140° C. for one minute. The polyimide film was then passed through a far-infrared heating furnace having an atmospheric temperature of 390° C. for 20 seconds to conduct imidization. Thus, adhesive layers composed of the thermoplastic polyimide precursor were formed. Thereby, a three-layer laminate in which adhesive layers were laminated on both surfaces of the polyimide film was prepared.

An 18- μ m rolled copper foil (manufactured by Japan Energy Corporation, trade name: BHY-22B-T) was disposed on each surface of the three-layer laminate, and a protective material (manufactured by Kaneka Corporation, trade name: Apical 125NPI) was applied on the surface of each copper foil. The resulting laminate was thermally laminated at a lamination temperature of 380° C., a lamination pressure of 196 N/cm (20 kgf/cm), and a lamination rate of 1.5 m/min while a tension of 0.4 N/cm was applied to the polyimide film. The hot lamination was continuously performed to produce a flexible metal-clad laminate.

After the lamination, the protective material was removed from the flexible metal-clad laminate. The above-described samples for measuring the rate of dimensional change were prepared from the flexible metal-clad laminate, and the rates of dimensional change before and after etching of each measurement sample were measured by the above method. The etching was performed with a device as follows. A hydrochloric acid solution (concentration: 30% or higher) of ferric chloride manufactured by Harima Kagaku Kogyo K.K. was heated to 30° C. with a heater, and the heated solution was sprayed from above and below the film to expose each surface of the film to the solution. The time of contact between the ferric chloride solution and the metal-clad laminate was set to within 10 minutes. In the etching process, the time was adjusted according to the etching rate. After the etching, the film was washed with water and dried by blowing off the droplets with air. Thus, a film with the copper layers removed was produced.

The rates of dimensional change of the polyimide film before and after etching were measured. The results are shown in Table 4. In Table 4, as in Tables 2 and 3, rows corresponding to an end portion, the central portion, and another end portion are provided for each example (or comparative example) to show the results of the measurement samples 51, 52, and 53.

As is apparent from the results, the polyimide film of the present invention had small rates of dimensional change and was suitable for a base film.

Example 2

A polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 4.40 and the TD expansion ratio

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was 4.40 as shown in Table 1. A flexible metal-clad laminate was produced as in Example 1 using the prepared polyimide film.

The physical property values of the polyimide film and the flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4. As is apparent from the results, the use of the polyimide film of the present invention reduced the rates of dimensional change after etching and stabilized the rates of dimensional change across the entire width.

The polyimide film had an elastic modulus of 5.9 GPa.

Example 3

A polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 3.90 and the TD expansion ratio was 0.00, and that the initial temperature in the tenter furnace was 130° C., and the film was further baked stepwise at 250° C., 350° C., 450° C., and 515° C. to conduct imidization, as shown in Table 1. A flexible metal-clad laminate was produced as in Example 1 using the prepared polyimide film.

The physical property values of the polyimide film and the flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4. As is apparent from the results, the use of the polyimide film of the present invention reduced the rates of dimensional change after etching and stabilized the rates of dimensional change across the entire width.

The polyimide film had an elastic modulus of 6.1 GPa.

Example 4

A polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 2.00 and the TD expansion ratio was 0.00, and that the initial temperature in the tenter furnace was 130° C., and the film was further baked stepwise at 250° C., 350° C., 450° C., and 515° C. to conduct imidization, as shown in Table 1. A flexible metal-clad laminate was produced as in Example 1 using the prepared polyimide film.

The physical property values of the polyimide film and the flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4. As is apparent from the results, the use of the polyimide film of the present invention reduced the rates of dimensional change after etching and stabilized the rates of dimensional change across the entire width.

The polyimide film had an elastic modulus of 5.8 GPa.

Example 5

A polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 4.00 and the TD expansion ratio was 0.00, and that the initial temperature in the tenter furnace was 160° C., and the film was further baked stepwise at 300° C., 450° C., and 515° C. to conduct imidization, as shown in Table 1. A flexible metal-clad laminate was produced as in Example 1 using the prepared polyimide film.

The physical property values of the polyimide film and the flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4. As is apparent from the results, the use of the polyimide film of the present invention reduced the rates of dimensional change after etching and stabilized the rates of dimensional change across the entire width.

The polyimide film had an elastic modulus of 6.0 GPa.

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Example 6

A polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 3.00 and the TD expansion ratio was 0.00, and that the initial temperature in the tenter furnace was 170° C., and the film was further baked stepwise at 300° C., 450° C., and 515° C. to conduct imidization, as shown in Table 1. A flexible metal-clad laminate was produced as in Example 1 using the prepared polyimide film.

The physical property values of the polyimide film and the flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4. As is apparent from the results, the use of the polyimide film of the present invention reduced the rates of dimensional change after etching and stabilized the rates of dimensional change across the entire width.

The polyimide film had an elastic modulus of 6.0 GPa.

Example 7

A polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 5.00 and the TD expansion ratio was 0.00, and that the initial temperature in the tenter furnace was 165° C., and the film was further baked stepwise at 300° C., 450° C., and 515° C. to conduct imidization, as shown in Table 1. A flexible metal-clad laminate was produced as in Example 1 using the prepared polyimide film.

The physical property values of the polyimide film and the flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4. As is apparent from the results, the use of the polyimide film of the present invention reduced the rates of dimensional change after etching and stabilized the rates of dimensional change across the entire width.

The polyimide film had an elastic modulus of 6.1 GPa.

Comparative Example 1

A comparative polyimide film was prepared as in Example 1 except that the TD shrinkage ratio was 0.00 and the TD expansion ratio was 0.00 as shown in Table 1 ("Comparative Example 1" in Table 1). A comparative flexible metal-clad laminate was produced as in Example 1 using the prepared comparative polyimide film.

The physical property values of the comparative polyimide film and the comparative flexible metal-clad laminate were evaluated by the same methods as those in Example 1. The results are shown in Tables 2 to 4 ("Comparative Example 1" in Tables 2, 3, and 4). As is apparent from the results, the use of the comparative polyimide film increased the rates of dimensional change after etching, and particularly increased the amounts of dimensional change in the D_R and D_L directions. Thus, it was evident that a flexible metal-clad laminate having stable rates of dimensional change across the entire width could not be obtained.

The polyimide film had an elastic modulus of 6.1 GPa.

TABLE 1

	Residual component ratio (%)	Initial tempera- ture in furnace (° C.)	Stretch- ing tempera- ture (° C.)	TD shrinkage ratio	TD expan- sion ratio
Example 1	54	177	450	4.40	2.20
Example 2	54	177	450	4.40	4.40

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TABLE 1-continued

	Residual component ratio (%)	Initial tempera- ture in furnace (° C.)	Stretch- ing tempera- ture (° C.)	TD shrinkage ratio	TD expansion ratio
Example 3	60	130	—	3.90	0.00
Example 4	60	130	—	2.00	0.00
Example 5	52	160	—	4.00	0.00
Example 6	71	170	—	3.00	0.00

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TABLE 1-continued

	Residual component ratio (%)	Initial tempera- ture in furnace (° C.)	Stretch- ing tempera- ture (° C.)	TD shrinkage ratio	TD expansion ratio
Example 7	68	165	—	5.00	0.00
Comparative	54	177	—	0.00	0.00
Example 1					

TABLE 2

		Coefficient of linear expansion						
		Difference						
			in	Direction		Average		
	Position	Molecular orientation angle (degrees)	molecular orientation angle (degree)	of molecular orientation	Perpendicular direction ppm/° C.	coefficient of linear expansion C _{LE} (ppm/° C.)	Coefficient of linear expansion ratio A	Difference A _{DIF} in coefficient of linear expansion ratio
Example 1	End	0	9	11.5	14.2	12.8	1.21	0.10
	Center	-3		12.0	13.6		1.13	
Example 2	End	6		11.3	14.1		1.22	0.12
	End	-5	16	9.59	16.74	13.1	1.54	
	Center	-1		10.3	15.9		1.43	
Example 3	End	11		10	15.8		1.45	0.02
	End	-1	6	10.1	14.1	12.8	1.33	
	Center	0		11.2	15.3		1.31	
Example 4	End	5		10.9	15.1		1.32	0.02
	End	-6	11	11.5	17.9	14.5	1.44	
	Center	1		11.4	18.1		1.45	
Example 5	End	5		10.9	17.3		1.45	0.05
	End	-3	17	9.6	18.2	13.5	1.62	
	Center	-6		8.6	17.3		1.67	
Example 6	End	11		9.1	18.1		1.66	0.09
	End	-13	26	11.2	15.3	13.3	1.31	
	Center	5		11.5	15		1.26	
Example 7	End	13		11.9	14.8		1.22	0.13
	End	-15	31	7.3	18	12.8	1.85	
	Center	10		7	18.4		1.90	
Comparative	End	16		8	17.9		1.76	0.49
	End	-45	90	8.66	17.2	12.6	1.66	
	Center	-6		10.59	12.92		1.20	
Example 1	End	45		8.67	17.73		1.69	

TABLE 3

		Tear propagation resistance			
	Position	Direction of molecular orientation	Perpendicular direction g/mm	Tear propagation resistance ratio TD/MD	Difference between the maximum and the minimum of tear propagation resistance ratio
Example 1	End	160	166	1.04	0.03
	Center	149	153	1.03	
Example 2	End	155	163	1.05	0.02
	End	156	171	1.10	
	Center	142	154	1.08	
Example 3	End	160	172	1.07	0.01
	End	141	147	1.05	
	Center	123	128	1.04	
Example 4	End	135	141	1.04	0.00
	End	152	163	1.07	
	Center	146	157	1.08	
Example 5	End	156	168	1.08	0.01
	End	160	178	1.11	
	Center	155	175	1.13	
	End	163	183	1.12	

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TABLE 3-continued

	Position	Tear propagation resistance		Tear propagation resistance ratio TD/MD	Difference between the maximum and the minimum of tear propagation resistance ratio
		Direction of molecular orientation	Perpendicular direction g/mm		
Example 6	End	155	160	1.03	0.02
	Center	148	155	1.05	
	End	156	162	1.04	
Example 7	End	150	177	1.18	0.07
	Center	140	175	1.25	
	End	154	182	1.18	
Comparative Example 1	End	131	147	1.12	0.12
	Center	120	122	1.01	
	End	135	153	1.13	

TABLE 4

Rate of dimensional change after etching						Reference Numerals	
	Position	MD	TD %	R	L		
Example 1	End	-0.03	-0.04	-0.01	-0.06	25	1 40 mm polyimide film
	Center	-0.03	-0.03	-0.03	-0.03		2 measurement sample (direction of molecular orientation axis)
	End	-0.03	-0.04	-0.01	-0.06		3 measurement sample (perpendicular direction)
Example 2	End	-0.03	-0.05	-0.04	-0.04	30	4 measurement part of elastic modulus
	Center	-0.02	-0.06	-0.05	-0.04		5 MD direction (mechanical feeding direction of film)
	End	-0.04	-0.04	-0.06	-0.02		10 positive (plus) molecular orientation angle
Example 3	End	-0.03	-0.05	-0.04	-0.03	35	11 negative (minus) molecular orientation angle
	Center	-0.04	-0.04	-0.05	-0.03		12 TD direction (direction perpendicular to mechanical feeding direction of film)
	End	-0.03	-0.05	-0.02	-0.02		13 MD direction
Example 4	End	-0.04	-0.02	-0.03	-0.04	40	14 TD direction
	Center	-0.04	0.00	-0.02	-0.02		15 molecular orientation axis
	End	-0.03	-0.02	-0.02	-0.03		20 sample film (direction of molecular orientation axis)
Example 5	End	0.02	-0.05	-0.01	0.00	45	21 sample film (direction perpendicular to molecular orientation axis)
	Center	0.03	-0.06	-0.03	0.01		22 direction perpendicular to molecular orientation axis
	End	0.04	-0.05	-0.02	0.02		23 10 mm
Example 6	End	-0.03	-0.04	-0.04	-0.03	50	24 10 mm
	Center	-0.04	-0.05	-0.03	-0.05		25 20 mm
	End	-0.03	-0.05	-0.02	-0.02		26 film transfer apparatus
Comparative Example 1	End	-0.03	0.02	0.09	-0.10	55	31 first heating furnace
	Center	-0.07	-0.01	0.00	0.02		32 second heating furnace
	End	-0.11	0.03	-0.10	0.07		33 third heating furnace
BRIEF DESCRIPTION OF THE DRAWINGS						60	34 fourth heating furnace
							35 fifth heating furnace
							36 film-gripping start position
							37 width X between gripping devices of film
							38 film width Y in the TD direction of gel film
							39 gripped by gripping devices
							40 film-transferring direction
							41 width Z between both fixed ends in the TD direction before stretching
							42 width W between both fixed ends after film is stretched in the TD direction in furnace
							43 unit (die) for casting or applying organic solvent solution
						65	44 base for applying organic solvent solution
							45 unit for applying tension to gel film
							46 position from which gel film is peeled off
							47 step of taking up to takeup unit (takeup unit of polyimide film)
							50 flexible metal-clad laminate
							51 measurement sample (an end portion)
							52 measurement sample (central portion)
							53 measurement sample (another end portion)
							60 hole for measurement

FIG. 1 shows a method of obtaining samples for determining the molecular orientation angle and the molecular orientation axis.

FIG. 2 shows a method of sampling films for measuring the coefficient of linear expansion.

FIG. 3 is a view illustrating the molecular orientation axis and the molecular orientation angle of a film.

FIG. 4 shows a method of sampling films for measuring the tear propagation resistance.

FIG. 5 includes schematic views showing a production process and a transfer process of a film.

FIG. 6 is a schematic view showing a state in which a film is gripped.

FIG. 7 is a schematic view showing positions of samples prepared from an FPC.

FIG. 8 is a schematic view showing positions for measuring dimensional changes of a sample for measuring the rates of dimensional change.

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The invention claimed is:

1. A polyimide film produced by a continuous process, wherein when a coefficient of linear expansion a in a direction of the molecular orientation axis and a coefficient of linear expansion b in a direction perpendicular to the molecular orientation axis are measured in the temperature range of 100° C. to 200° C., a coefficient of linear expansion ratio A represented by equation (1):

$$A=1+\{(b-a)/(b+a)\} \times 2 \quad (1)$$

is in the range of 1.13 to 3.00 across the entire width.

2. The polyimide film according to claim 1, wherein the difference between the maximum A_{MAX} and the minimum A_{MIN} of the coefficient of linear expansion ratio A is 0.30 or less.

3. The polyimide film according to claim 1, wherein the difference between the maximum and the minimum of the molecular orientation angle of the polyimide film is 40° or less across the entire width.

4. The polyimide film according to claim 1, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle is within 0±20°.

5. The polyimide film according to claim 1, wherein the average coefficient of linear expansion in the temperature range of 100° C. to 200° C. is in the range of 5.0 to 25.0 ppm/° C.

6. A laminate comprising the polyimide film according to claim 1.

7. The laminate according to claim 6, further comprising at least a metal layer.

8. A flexible printed circuit board comprising the polyimide film according to claim 1 as a base film.

9. A polyimide film produced by a continuous process, wherein when a tear propagation resistance c in a direction of the molecular orientation axis and a tear propagation resistance d in a direction perpendicular to the molecular orientation axis are measured, the tear propagation resistance ratio d/c is in the range of 1.01 to 1.20 and the difference between

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the maximum and the minimum of the tear propagation resistance ratio d/c is 0.10 or less across the entire width.

10. The polyimide film according to claim 9, wherein the difference between the maximum and the minimum of the molecular orientation angle of the polyimide film is 40° or less across the entire width.

11. The polyimide film according to claim 9, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle of the polyimide film is within 0±20° across the entire width.

12. A laminate comprising the polyimide film according to claim 9.

13. The laminate according to claim 12, further comprising at least a metal layer.

14. A flexible printed circuit board comprising the polyimide film according to claim 9 as a base film.

15. The polyimide film according to claim 2, wherein the difference between the maximum and the minimum of the molecular orientation angle of the polyimide film is 40° or less across the entire width.

16. The polyimide film according to claim 2, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle is within 0±20°.

17. The polyimide film according to claim 3, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle is within 0±20°.

18. A laminate comprising the polyimide film according to claim 4.

19. A laminate comprising the polyimide film according to claim 5.

20. The polyimide film according to claim 10, wherein when the transferring direction (MD direction) during the continuous production is defined as 0°, the molecular orientation angle of the polyimide film is within 0±20° across the entire width.

* * * * *

EXHIBIT C

United States Patent [19]**Kawaratani et al.**[11] **Patent Number:** **5,075,064**[45] **Date of Patent:** **Dec. 24, 1991**[54] **METHOD AND APPARATUS FOR
CONTINUOUSLY PRODUCING RESIN
FILMS AND INSTALLATION THEREFOR**[75] **Inventors:** Haruo Kawaratani; Tetsuo Yoshioka,
both of Ohtsu, Japan[73] **Assignee:** Kanegafuchi Kagaku Kogyo
Kabushiki Kaisha, Osaka, Japan[21] **Appl. No.:** 493,316[22] **Filed:** Mar. 14, 1990[30] **Foreign Application Priority Data**

Mar. 14, 1989 [JP] Japan 1-62838

[51] **Int. Cl.⁵** B29C 41/50[52] **U.S. Cl.** 264/205; 264/216;
264/345; 425/74; 425/75; 425/224[58] **Field of Search** 264/216, 212, 345, 169,
264/204, 205; 425/224, 74, 75, 445[56] **References Cited****U.S. PATENT DOCUMENTS**

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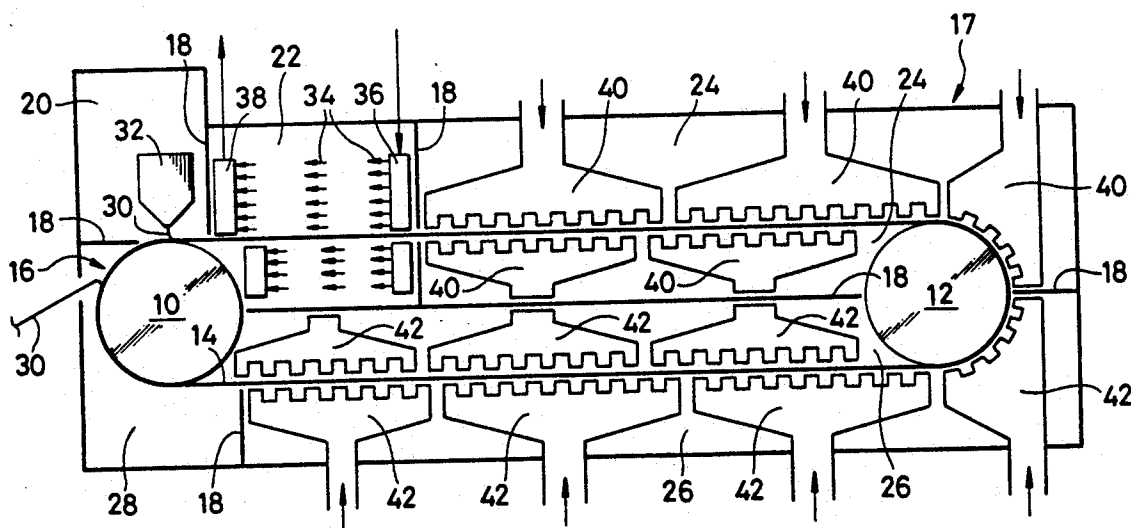
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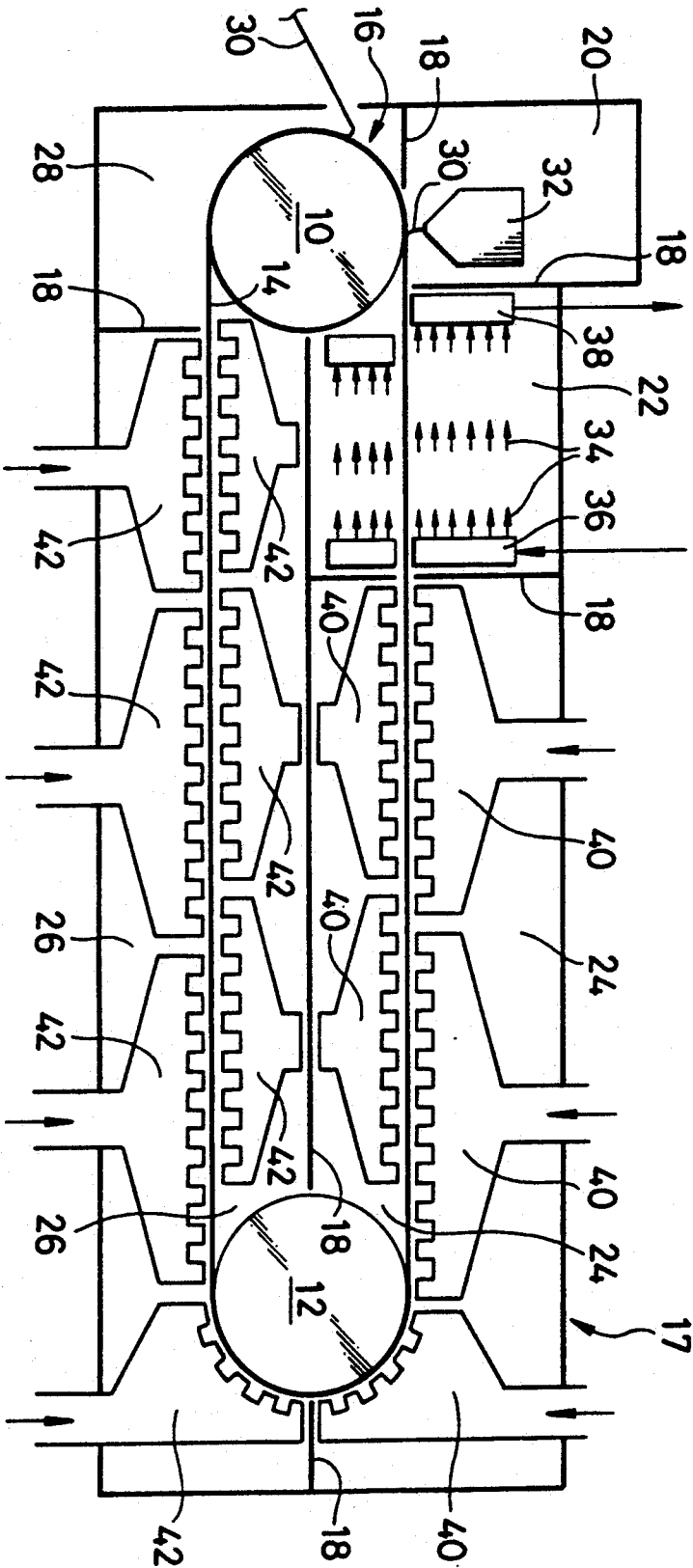
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Primary Examiner—Jeffery Thurlow*Attorney, Agent, or Firm*—Cushman, Darby & Cushman[57] **ABSTRACT**

For continuous production of a resin film having a plain surface, a resin solution cast in film form over an endless belt is pre-hardened by a gas stream supplied for flow in a direction generally parallel to the surface of the endless belt, and then a jet of gas is blown in the direction of movement of the endless belt whereby the resin is hardened. In the process for resin film production wherein the resin film is cast over the endless belt and then pre-hardened by a parallel gas stream, the cast film being then hardened by a jet of gas, the installation for production is divided by partitions so as to enable various stages to be operated independently.

6 Claims, 1 Drawing Sheet



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METHOD AND APPARATUS FOR CONTINUOUSLY PRODUCING RESIN FILMS AND INSTALLATION THEREFOR

BACKGROUND OF THE INVENTION

This invention relates to a method and apparatus for continuously producing resin films and also to an installation therefor.

Hitherto, resin films have been produced by casting a resin solution in film form over a casting drum through extrusion or coating, or casting the resin solution likewise over an endless belt in order to allow it to set and become hardened, then blowing hot air onto the film-form cast resin to allow the cast resin to become hardened to a self-supportable level, and subsequently separating the film-form resin from the casting drum or endless belt.

However, when hot air as blown in a jet stream through a nozzle or the like is applied to the surface of the film-form resin solution cast over the endless belt or the like surface, the surface of the resin film is often subject to the trouble of wind ripples being formed thereon under the force of the hot air, even if the resin solution is of high viscosity of, for example, 100 to 1000 poise. Another problem is that when hot air is blown through a nozzle onto the resin film cast over the endless belt, the cast resin film is subject to temperature irregularity in the transverse direction thereof because of the endless belt is continuously moving, with the result that no uniformity can be obtained in setting and hardening speed, surface irregularity being thus caused to the resin film. Such wind ripples and surface irregularity due to temperature unevenness will pose no problem in case where the resin film is used for foodstuff wrapping or the like purposes, but where it is used with electronic parts and the like, it will affect the electromagnetic characteristics of those parts.

The pulleys over which the endless belt is trained are heated by the hot air blown for setting and hardening the cast resin and accordingly the temperature of the endless belt itself is high because of heat transfer from the heated pulleys. Therefore, when a resin solution of, for example, the reactive setting type is cast in film form, setting and drying will occur with the film form resin simultaneously in parallel and randomly. This has made it difficult to control both the setting reaction speed and drying speed of the resin.

BRIEF SUMMARY

The object of this invention is to provide a novel method for continuously producing a resin film having a plain surface in a steady and efficient manner, and an apparatus and installation for carrying out the method.

According to the invention, there is provided a method for continuously producing a resin film which comprises: (a) a casting stage for continuously extruding or coating a resin solution in film form for casting it over an endlessly rotating plain surface, (b) a parallel-stream hardening stage for pre-hardening the cast resin film by heating and exposing it to a gas stream fed in a direction substantially parallel to the resin film, (c) a jet hardening stage or stages for hardening the pre-hardened resin film from the parallel-stream hardening stage by heating and exposing it to a jet of gas blown toward the resin film thereby to harden the resin film at least to a self-supporting level, and (d) a separation stage for

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separating from the plain surface the resin film which has passed through the jet hardening stage.

In such method for continuously producing a resin film, the endlessly rotating surface is an endless belt or casting drum.

In such method for continuously producing a resin film, the gas stream by which the resin film is heated and which is fed in a direction substantially parallel to the resin film in the parallel-stream hardening stage is a hot air stream.

According to the invention, there is provided an apparatus for continuously producing a resin film according to the above method, the apparatus comprising: (a) casting and transport means including two pulleys and an endless belt coursed for continuous run between the two pulleys for casting a resin solution in film form over the endless belt and transporting same thereon, (b) parallel stream hardening means for heating the cast resin film and exposing it to a gas stream fed substantially parallel to the resin film to thereby harden the resin film to a non-fluid state, (c) one-stage or multistage jet hardening means for heating the resin film hardened to a non-fluid state and exposing it to a jet of gas blown toward the resin film thereby to harden the resin film to a self-supporting level, and (d) separating means for separating the resin film hardened to a self-supporting level from the endless belt.

According to the invention, there is also provided an apparatus for continuously producing a resin film including casting and transport means having two pulleys and an endless belt coursed for continuous run between the two pulleys for casting a resin solution in film form over the endless belt, the apparatus comprising the pulley disposed nearer to the casting means being provided with cooling means for cooling the pulley to thereby cool the endless belt.

Further, according to the invention, there is provided an installation for continuously producing a resin film wherein a resin solution is cast in film form over an endless belt coursed for continuous run between two pulleys, the cast resin film being hardened to a self-supporting level, the resin film being then separated from the endless belt, comprising: (a) a casting chamber for casting the resin solution in film form over the endless belt, (b) a parallel stream hardening chamber for heating the cast resin film and exposing it to a gas stream substantially parallel to the resin film thereby to harden the resin film at least to a non-fluid state, (c) a jet hardening chamber having one or more compartments for heating the resin film hardened to a non-fluid state and exposing it to a jet of gas blown toward the resin film at least to a self-supporting level, and (d) a separating chamber for separating the resin film hardened to a self-supporting level from the endless belt.

In such installation for continuously producing a resin film, a dehumidifying stream of gas having a dew point lower than the temperature of the resin solution is supplied into the casting chamber.

According to the invention, the resin solution cast in film form over the endless belt is transported to the next stage in which it is uniformly heated on the one hand, while on the other hand volatiles produced in the course of setting reaction of the resin and some organic solvent are caused to evaporate by the gas stream fed generally parallel to the surface of the resin film. After the resin film is pre-hardened in the parallel-stream hardening stage until it has lost its fluidity, the resin film is transported to the next stage, i.e., jet hardening stage.

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In the jet hardening stage, the resin film hardened to such non-fluid state is heated continuously in a single stage or stepwise in a plurality of stages and is exposed to a jet of gas blown through a nozzle in a single stage or in a plurality of stages so that volatiles produced in the course of setting reaction of the resin and some organic solvent can be efficiently caused to evaporate. The resin film which has thus been hardened and dried to a self-supporting level is then transported to the separation stage in which it is separated from the endless belt and finally taken up as a product onto a roll or the like.

Of the pulleys over which the endless belt is trained, the one pulley disposed nearer to the casting means is provided with cooling means so that the endless belt can be cooled through the pulley to any desired temperature. Through this arrangement it is possible to prevent any abrupt setting reaction of the resin film cast over the endless belt and to control the setting reaction of the resin film. Further, it is possible to control to an optimum value the evaporation rate of volatiles produced in the course of setting reaction of the resin film as well as of organic solvent contained in the resin.

The installation for continuously producing a resin film is provided with partitions for dividing the installation into a plurality of chambers, including casting chamber, parallel-stream hardening chamber, one or more jet hardening chambers, and separation chamber, so that operations of the different stages can be carried out within separate chambers. Through this arrangement, the operating atmosphere can easily be adjusted to suit each stage. Operation in each stage is unlikely to be affected by operation in adjacent stages. The possibility of wind ripples being formed on the resin film surface is eliminated. Further, the arrangement facilitates the control of setting reaction of the resin film and the control of the rate of fly-off of volatiles produced in the course of such reaction and organic solvents.

According to the invention, the resin film cast over the endless belt is heated and hardened by a stream of gas fed in parallel relation thereto to the extent that the resin film no longer has fluidity; and then it is hardened through exposure to a jet of gas until it attains good self-supporting characteristics. Therefore, the resin film is not liable to wind ripples being formed on its surface and thus a resin film having a plain surface can be produced.

The endless belt on which a resin film is cast is pre-cooled to an optimum temperature. This enables easy control of resin setting reaction and also of evaporation of volatiles produced in the course of such reaction and organic solvent content of the resin for causing such substances to evaporate under optimum conditions.

Moreover, the resin film producing installation is provided with partitions for defining the individual operating chambers so as to enable operations in various stages to be carried out in separate chambers. Therefore, resin film production can be carried out under optimum conditions through suitable stage-by-stage adjustment of operating atmosphere.

BRIEF DESCRIPTION OF THE DRAWING

The single FIGURE is a schematic diagram for explanation of the method, apparatus, and installation for continuously producing a resin film according to the invention.

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DETAILED DESCRIPTION OF THE INVENTION

One embodiment of the invention will now be described in detail with reference to the drawing.

The single FIGURE is an explanatory diagram which shows general arrangement of the installation for continuously producing a resin film according to the invention. In the drawing, a transport unit 16 comprises pulleys 10 and 12, and an endless belt 14 trained over the pulleys 10, 12. The transport unit 16 is arranged in a space enclosed by outer walls 17 in such way that it extends through various chambers, including a casting chamber 20, a parallel-stream hardening chamber 22, a first jet hardening chamber 24, a second jet hardening chamber 26, and a separating chamber 28, which are separately defined by partitions 18 dividing the space interior of the outer walls 17.

The pulley 10 of the transport unit 16 is drivably rotated by a drive unit not shown so as to rotate, in conjunction with the driven pulley 12, the endless belt 14 trained over the pulleys 10, 12. In the interior of the pulley 10 is disposed a cooling water conduit not shown which serves as cooling means for the pulley 10. The temperature at which the pulley 10 is to be maintained is suitably selected according to the type of the resin film to be produced. For example, where polyamide is produced through cyclic reaction of polyamide acid in order to produce a polyamide film, the temperature of the pulley 10 is kept at about 50° C. That is, the temperature of the pulley 10 should be such that the pulley 10 can easily be heated up to a temperature suitable for accelerating the setting reaction of the resin solution cast in film form over the endless belt 14 and further such that at the temperature the resin solution cast over the endless belt 14 can easily start setting reaction but volatiles produced in conjunction with the reaction and organic solvents cannot easily fly off.

The driven pulley 12 is of such arrangement that its width is smaller than the width of the endless belt 14 and that bearings not shown in which the pulley 12 is rotatably supported at its ends are so fixed to the floor as to be shift-adjustable in the direction of travel of the endless belt 14. The bearings are separately shiftable relative to the endless belt 14 so that snaking of the endless belt 14 can be corrected by changing the tension of the endless belt 14 at both ends through the pulley 12. Since the width of the pulley 12 is smaller than that of the endless belt 14, corners of the pulley 12 at both ends act on the endless belt 14 to cause the endless belt 14 to stop snaking by merely adjusting the bearings.

The endless belt 14 is formed of stainless steel, aluminum alloy, or the like material, and its surface is polished to mirror surface to permit production of a plain resin film.

In the casting chamber 20 located adjacent the drive pulley 10 of the transport unit 16 there is provided a die 32 for extruding resin solution 30 into a film form of uniform thickness, with the arrangement that resins of the reaction setting type are mixed in a mixer and fed to the die 32. The die 32 is cooled to a low temperature in order to prevent the pot life (serviceable life) of mixed reaction setting type resins from lapsing away within the die 32. Therefore, the surface of the die 32 is liable to condensation. To avoid such condensation, a dehumidifying gas of a temperature lower than the dew point of the die 32 is fed into the casting chamber 20.

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The resin film 30 cast in film form through extrusion over the endless belt 14 is of a viscosity range of 10 to 1000's poise. When the surface of the resin film 30 is exposed directly to a jet of gas, however, wind ripples are easily formed on the film surface and set as they are, even if the resin film 30 is of high viscosity, with the result that a resin film 30 bearing irregular marks on its surface is produced. According to the invention, therefore, resin film 30 cast over the endless belt 14 is transported to the parallel-stream hardening chamber 22 in which the resin film 30 is set and hardened in such a way that no wind ripple may be formed on the film surface.

The parallel-stream hardening chamber 22 is a chamber defined across the endless belt 14. In the parallel-stream hardening chamber 22 are disposed a blowing box 36 for blowing hot air 34 in a direction parallel to the surface of the resin film 30 (endless belt 14) and a suction box 38 for discharging outward the hot air 34 blown from the blowing box 36 and volatiles evaporated from the resin film 30. Therefore, the resin film 30 is uniformly heated by the hot air 34 blown from the blowing box 36 and, at same time, evaporation of volatiles, etc. is accelerated by the parallel stream of air (34). Hot air 34 blown from the blowing box 36 may be of the following conditions, for example: 90° C. in temperature, and 1-5 m sec in velocity. It is noted, however, conditions may vary according to the type of the resin.

After the surface of the resin film 30 is set and hardened to non-fluid state, the resin film 30 is exposed to a jet of hot air by which it is hardened to a self-supporting level.

In the present embodiment, hardening of resin film 30 by a hot air jet is carried out in two stages. That is, hardening operation for resin film 30 is carried out in a first jet hardening chamber 24 and a second jet hardening chamber 26. The jet hardening chamber 24, 26 are defined by partition 18 in the endless belt 14 at inner and outer sides thereof. In each of the chambers 24, 26 there is disposed a jet hardening unit 40, 42 equipped with a multiplicity of nozzles through which hot air is blown in jets toward the surface of the resin film 30 (endless belt 14). The resin film 30 is heated at both sides by hot air blown from the jet hardening units 40, 42 directly to the resin film 30 (endless belt 14), and volatiles produced in the course of setting reaction of the resin and organic solvent components contained therein are efficiently evaporated by the jet stream. Thus, the resin film 30 is hardened to a self-supporting level.

The temperature and velocity of a jet stream blown from the jet hardening chamber 40, 42 are preferably raised as the resin film progressively become hardened. For example, a jet stream blown from the jet hardening unit 40 in the first jet hardening chamber 24 has a temperature of 100° C. and a velocity of 10 m/sec and a jet stream from the jet hardening unit 42 in the second jet hardening unit 42 has a temperature of 110° C. and a velocity of 12 m/sec. The temperature and velocity values shown above are merely exemplary and not restrictive.

The resin film 30 thus hardened on the endless belt 14 to a self-supporting level is transported to the separation chamber 28 in which it is stripped by a stripping roller not shown from the endless belt 14 and wound onto a roll. The endless belt 14 from which the resin film 30 is separated is cooled by the cooling means provided within the drive pulley 10 and is then employed for a next cycle of operation for production of resin film 30.

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The endless belt 14 is already cooled through the pulley 10, so that when the resin solution (30) is cast in film form on the endless belt 14, the film form resin (30) is prevented from being momentarily heated to cause organic solvent and the like to evaporate from the surface of contact with the endless belt 14.

In this embodiment, as described above, the resin film cast on the endless belt is first set and hardened uniformly by a parallel stream of hot air to a non-fluid state, and then it is efficiently hardened by a jet of hot air to a self-supporting level. Therefore, the possibility of wind ripples being formed on the resin film surface is eliminated and thus a resin film having plain surface can be steadily produced. Moreover, each stage of operation is partitioned from adjacent stages so that operation can be carried out without disturbance from adjacent stages of operation. Thus, resin film production can be carried out in an optimum atmosphere and under optimum operation control.

One embodiment of the invention has been described above. It is noted, however, that the invention may be carried out in other forms.

For example, the parallel-stream hardening unit (36, 38) in the parallel-stream hardening chamber 22 may be disposed on the side facing the resin film 30 cast over the endless belt 14, while the jet hardening unit 40, 42 may be disposed on the side facing the endless belt 14. In that case, the surface of the resin film 30 is not liable to be exposed directly to air jet, there being thus no possibility of air ripples being formed.

The parallel-stream hardening unit may not be limited to one for hot air blowing. A heating source and a parallel stream source may be employed separately. For example, it is possible to employ an infrared or far-infrared generating unit to carry out uniform and steady heating of the resin film 30 cast over the endless belt 14 and, at the same time, to feed a stream of gas at ordinary temperatures in a direction parallel to the resin film 30. In this case, it is also possible to provide a stream of gas parallel to the resin film 30 through suction of the air within the parallel-stream hardening chamber and not by positive feed of air. The direction of flow of the parallel stream is not limited to a direction counter to the direction of movement of the endless belt 14; it may be same as the direction of movement of the endless belt 14 or a direction normal to the direction of movement of the endless belt 14.

Similarly, for the jet hardening unit, a heating source and a jet air may be employed separately.

One jet hardening chamber may be used instead of two. Treatment of the resin film by the jet hardening unit may be given one time only. It is also possible to provide a number of jet hardening chambers for step-by-step heating up, with a final stage for cooling. Again it is possible to arrange for feed of dehumidifying gas at a suitable location or locations so as to ensure that the resin film can be free from the adverse effect of condensation, within the installation, of gases evaporated from the resin.

The surface over which a resin solution is cast in film form through extrusion or coating and which is endlessly rotated is not limited to endless belt. It may be a casting drum having a reasonable radius of curvature. For resin solution casting, a coating method incorporating printing technique may be used as well as extruding technique. For pulley cooling, air cooling may be employed. This invention may be carried out in various modified, amended, or improved forms on the basis of

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the knowledge of any person skilled in the art and within the concept and spirit of the invention.

What is claimed is:

1. A method for continuously producing a resin film comprising the steps of:

casting a resin solution over an endlessly rotating plain surface to form a cast resin film thereon;

parallel-stream pre-hardening said cast resin film by heating and exposing said film to a gas stream fed in a direction substantially parallel to said film over the entire zone where said parallel-stream hardening step is performed;

jet hardening said cast resin film, which has been parallel-stream hardened, by heating and exposing said film to a jet of gas blown toward said cast resin film over the entire zone where said jet hardening step is performed, thereby hardening said film at least to a self-supporting level; and

separating said cast resin film which has been jet hardened from said plain surface.

2. A method for continuously casting a resin film as set forth in claim 1, wherein the endlessly rotating surface is an endless belt or casting drum.

3. A method for continuously casting a resin film as set forth in claim 1 or 2, wherein the gas stream by which the resin film is heated and which is fed in a direction substantially parallel to the resin film in the parallel-stream hardening stage is a hot air stream.

4. An apparatus for continuously producing a resin film comprising:

casting and transport means including a casting chamber for extruding resin solution of uniform thickness over an endless belt which is transported by two pulleys in such a way that said endless belt is coursed for continuous run between the two pulleys and resin solution is continuously cast in film form over the endless belt and transported thereon;

parallel stream hardening means including a parallel stream hardening chamber for heating the cast resin film and exposing said film to a gas stream fed substantially parallel to said film over the entire length of said endless belt passing through said

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parallel stream hardening chamber to thereby harden said film to a non-fluid state;

one-stage or multistage jet hardening means including a jet hardening chamber or chambers for heating the resin film hardened to a non-fluid state and means of exposing said film to a jet of gas blown toward said film over the entire length of said endless belt passing through said jet hardening chamber, thereby to harden said film to a self-supporting level; and

separating means including a separating chamber for separating the resin film hardened to a self-supporting level from said endless belt.

5. An installation for continuously producing a resin film wherein a resin solution is cast in film form over an endless belt coursed for continuous run between two pulleys, the cast resin film being hardened to a self-supporting level, the resin film being then separated from the endless belt, comprising:

a casting chamber for casting the resin solution in film form over said endless belt in such a way that said endless belt is coursed for continuous run between said two pulleys;

a parallel stream hardening chamber for heating the cast resin film and means for exposing said film to a gas stream fed substantially parallel to said film over the entire length of said endless belt passing through said parallel stream hardening chamber, thereby to harden said film at least to a non-fluid state;

a jet hardening chamber having one or more compartments for heating the resin film hardened to a non-fluid state and means for exposing it to a jet of gas blown toward said film over the entire length of said endless belt passing through said jet hardening chamber, to thereby harden said film at least to a self-supporting level; and

a separating chamber for separating the resin film hardened to a self-supporting level from said endless belt.

6. An installation for continuously producing a resin film as set forth in claim 5, wherein a dehumidifying stream of gas having a dew point lower than the temperature of the resin solution is supplied into the casting chamber.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,075,064

DATED : December 24, 1991

INVENTOR(S) : KAWARATANI, Haruo; YOSHIOKA, Tetsuo

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, line 27, change "polyamide" to --polyimide--; and
line 29, change "polyamide" to --polyimide--.

Signed and Sealed this
Third Day of August, 1993

Attest:



MICHAEL K. KIRK

Attesting Officer

Acting Commissioner of Patents and Trademarks

EXHIBIT D



US006264866B1

(12) **United States Patent**
Yamada et al.

(10) **Patent No.:** **US 6,264,866 B1**
(45) **Date of Patent:** ***Jul. 24, 2001**

(54) **METHOD FOR PRODUCING POLYIMIDE FILM**

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(73) **Assignee:** **Kanegafuchi Kagaku Kogyo Kabushiki Kaisha**, Osaka (JP)

(*) **Notice:** This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** **09/095,129**

(22) **Filed:** **Jun. 10, 1998**

(30) **Foreign Application Priority Data**

Jun. 11, 1997 (JP) 9-153587

(51) **Int. Cl.⁷** **B29C 39/14; B29C 41/24**
(52) **U.S. Cl.** **264/216; 264/204; 264/236; 264/331.19; 264/347**

(58) **Field of Search** 264/216, 204, 264/236, 331.21, 347, 331.19

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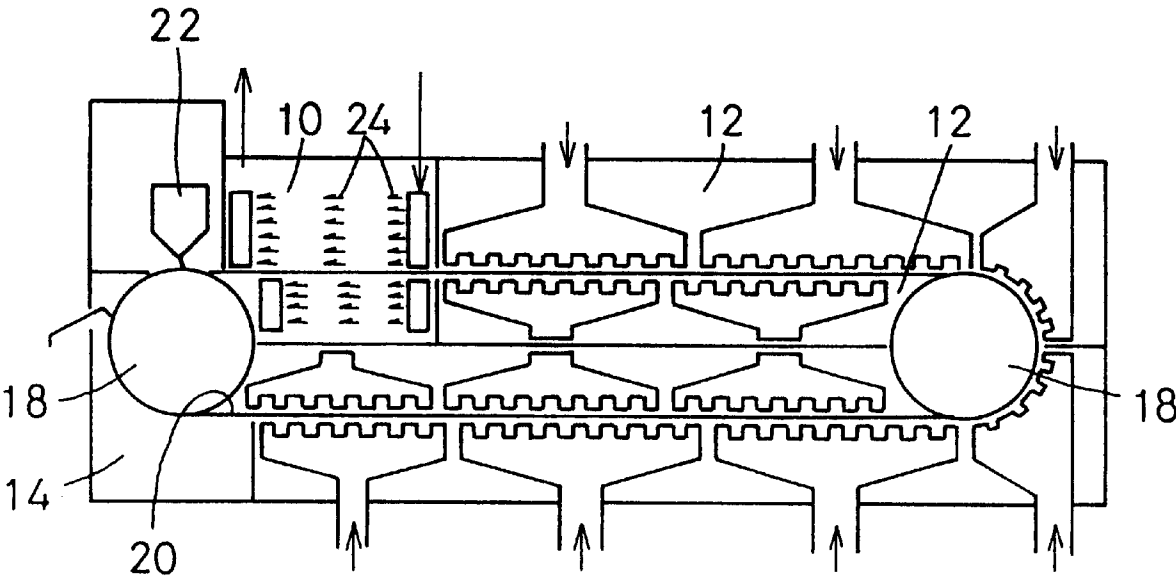
Primary Examiner—Mathieu D. Vargot

(74) *Attorney, Agent, or Firm*—Pillsbury Winthrop LLP

(57) **ABSTRACT**

A method for producing a polyimide film in which the imidation ratio and/or the amount of volatile constituent are controlled to improve the adhesive strength of the polyimide film. The method may also comprise controlling the highest temperature of heating the prefilm to improve the adhesive strength of the polyimide film.

14 Claims, 3 Drawing Sheets



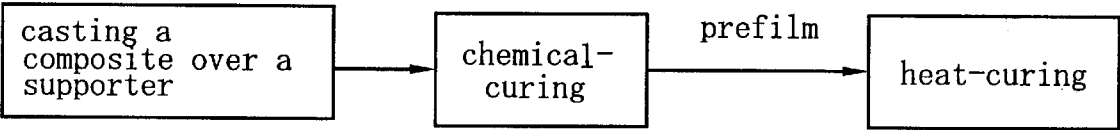


Fig.1

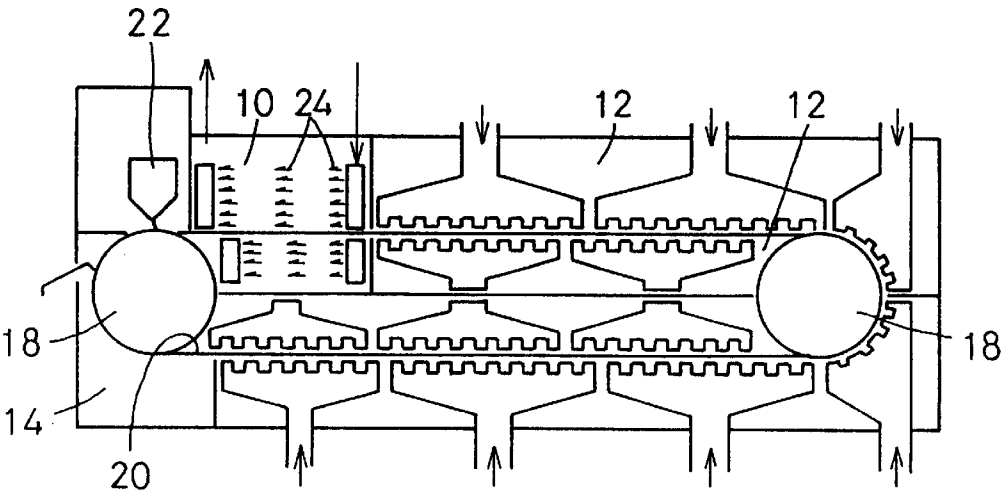


Fig.2

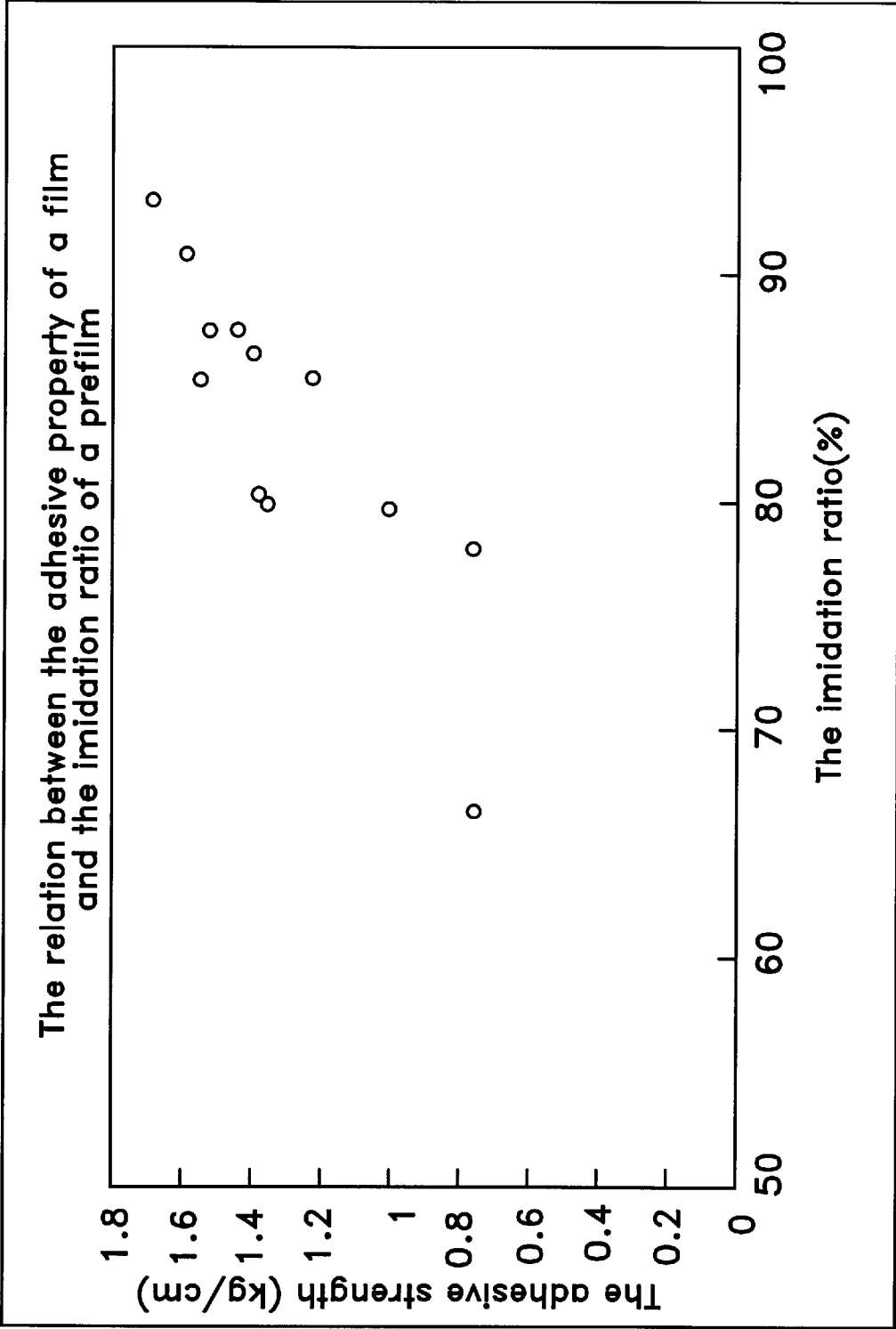


Fig.3

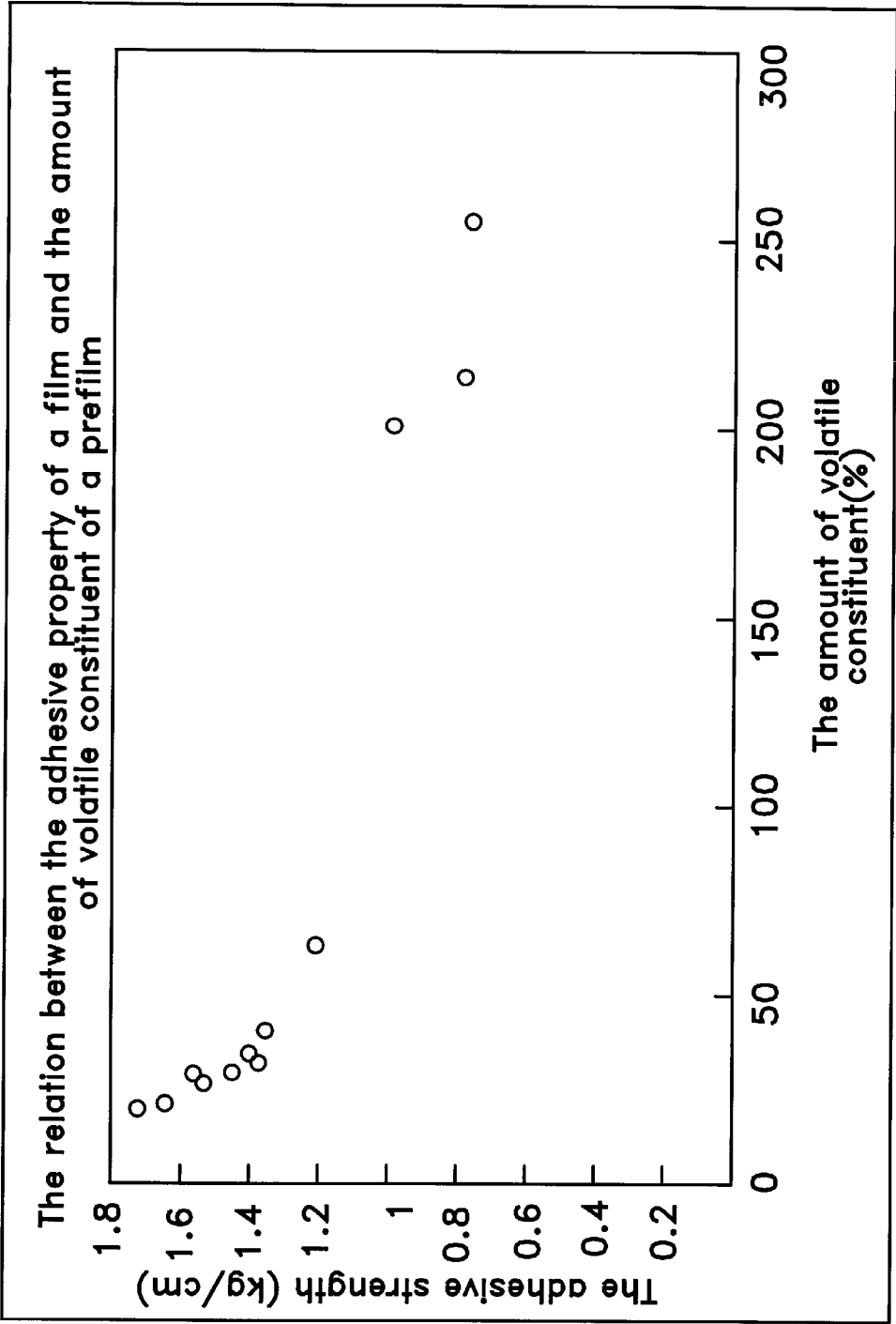


Fig.4

METHOD FOR PRODUCING POLYIMIDE FILM

BACKGROUND OF THE INVENTION

1. Field of Invention

The present invention relates to a method for producing a polyimide film, more particularly, to a method for producing a polyimide film by means of controlling its adhesive property.

2. Disclosure of the Related Art

As is commonly known, a polyimide film has various excellent properties such as heat-resistance, cold resistance, chemical-resistance, insulation and mechanical strength. Therefore, a polyimide film is widely used as such materials as an electric insulating film, a heat insulating film and a base film of flexible printed wiring board. In order to use a polyimide film for various purposes, a copper-clad laminated board is produced by superposing a layer of adhesive agent and copper foil on one or a both sides of a polyimide film, a pre-impregnated film (pregreg) is produced by coating a polyimide film with adhesive agent, or a composite film is produced by laminating fluorocarbon resin on a polyimide film. The adhesive strength is one of the important properties of a film, so that various attempts to improve the adhesive strength of a film have been made.

In order to provide the adhesive strength to a surface of a polymeric film, there are various techniques such as flame treatment for a film surface, corona discharge treatment, ultraviolet treatment, alkaline treatment, primer treatment, sand blast treatment and plasma treatment. For the purpose of providing the adhesive strength to a polyimide film without spoiling its other properties, one or more of the above-mentioned treatments are selected. These treatments are considered to be used for removing a weak boundary layer, which is formed on the film surface in the course of solvent-cast process and lowers the adhesive strength of a film.

All of the above-mentioned treatments are executed after producing a film to improve the adhesive strength of a finished film. The adhesive strength of a finished film is not constant. The above-mentioned after-treatments are also unstable. Therefore, it is difficult to stably provide a film with an improved adhesive strength by a prior art method. There is also an inevitable problem that the cost goes up due to the additional step to improve an adhesive property of a finished film. Same troubles and problems also occur in the course of producing a composite of a polyimide film and fluorocarbon resin. Thus, it has been difficult to constantly provide high adhesive strength to a film by using the conventional methods.

OBJECTS AND SUMMARY OF THE INVENTION

As the result of our researches to remove the above disadvantages and to stably provide a film with a high adhesive strength, we have eventually found the method for producing a film having an excellent adhesive property in which an adhesive property is controlled in course of producing a film. In the conventional method, an adhesive property of a film is improved by way of treating the surface of a finished film, however, in the present invention, an excellent adhesive property is incorporated in course of producing a film.

The method for producing a polyimide film according to the present invention, which overcomes the above-discussed

and numerous other disadvantages and deficiencies of the prior art, comprising the steps of i) casting a composition into a film shape, wherein said composition consists substantially of organic solvent solution of polyamide acid; ii) heating the film-shaped composition to obtain a prefilm with an adjusted imidation ratio and/or an adjusted amount of volatile constituent; and iii) further heating said prefilm to obtain a polyimide film.

The adjusted imidation ratio of the prefilm can be 70% or more.

The adjusted amount of volatile constituent of the prefilm can be 40 weight % or less.

The adjusted imidation ratio of the prefilm can be 70% or more and the adjusted amount of volatile constituent of the prefilm can be 40 weight % or less.

The highest temperature of heating a prefilm can be in a range from 450° C. to 630° C.

Thus, the present invention disclosed herein makes possible the objectives of (1) providing an adhesive property directly to a polyimide film; (2) providing an adhesive property extremely stably to a polyimide film for the purpose of overcoming uneven quality of adhesiveness and sudden loss of adhesiveness, which are often the case with conventional methods for providing adhesiveness to a finished film; and (3) maintaining a high value of the adhesive strength of a composite film obtained by laminating fluorocarbon resin on a polyimide film.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a flowchart of the present method for producing a polyimide film with an excellent adhesive property.

FIG. 2 is an example of the belt chamber according to the present invention.

FIG. 3 is a graph showing the relation between the amount of volatile constituent of a prefilm and the adhesive strength of a finished product. (The imidation ratio is not fixed.)

FIG. 4 is a graph showing the relation between the imidation ratio of a prefilm and the adhesive strength of a finished product. (The amount of volatile constituent is not fixed.)

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A “prefilm” used herein means a gel-state film hardened to such an extent that it can support itself after allowing a composition including the solvent solution of precursor of polyimide to flow from a die and then placing it on a supporter consecutively (in other words, casting the composition over the supporter); and evaporating a solvent or a reaction product to promote the imidation. The above-mentioned composition including the solvent solution of precursor of polyimide consists substantially of organic solvent solution of polyamide acid.

The preferred embodiments of the present method for producing a film with an excellent adhesive property are described below.

Generally, a polyimide film is insoluble and infusible, so that a solvent casting method, in which organic solvent solution of precursor of polyimide is cast over a supporter such as a drum and a belt, is used for producing a polyimide film. The solvent casting method is also used in the present invention.

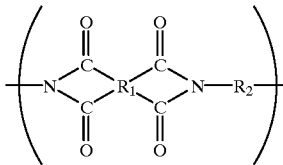
A polyimide film produced by using the present method can be obtained from well-known materials, e.g., from one

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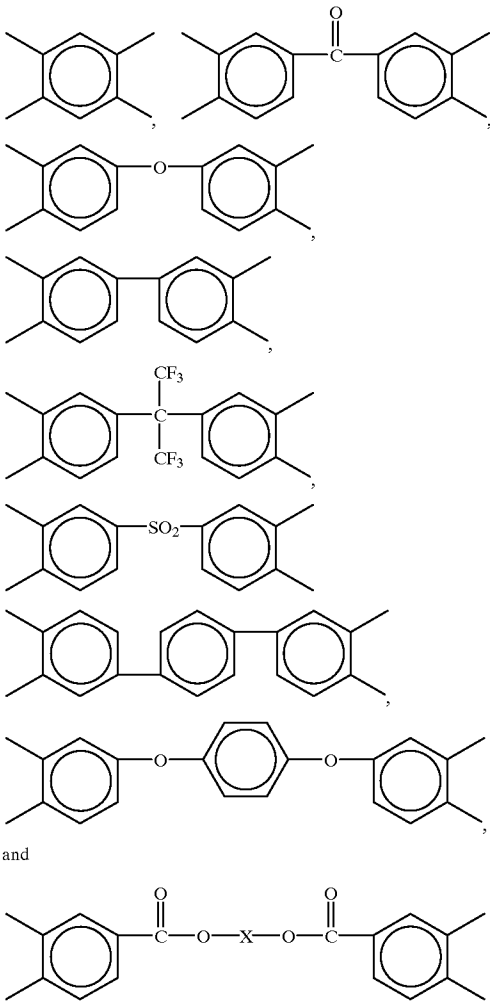
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or more organic tetracarboxylic dianhydrides and one or more diamines.

In the present invention, the term “a polyimide film” is interpreted in a broad sense, including polyimide, polyamideimide, polyetherimide and polyesterimide films. The term includes polyimide films of non-thermoplasticity, thermoplasticity and thermosetting. In other words, molecular structure of polyimide is not restricted in the present invention. However, it is preferable that a polyimide consists of a repeating unit of the general formula (1):

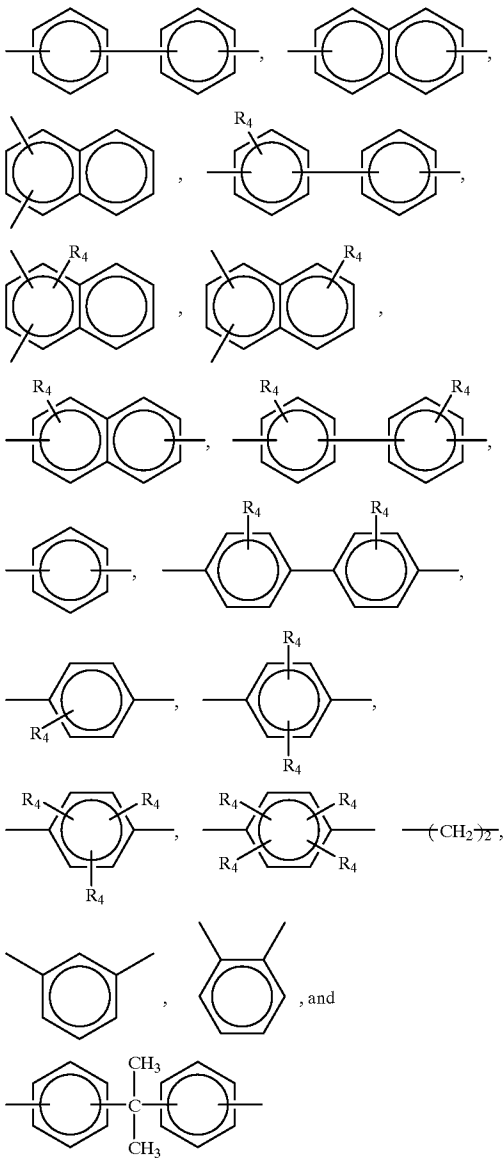


wherein R₁ is a tetravalent organic group. Concretely, R₁ has at least one benzene, which bonds directly to an adjoining carbonyl group. More concretely, R₁ is at least one selected from the group consisting of



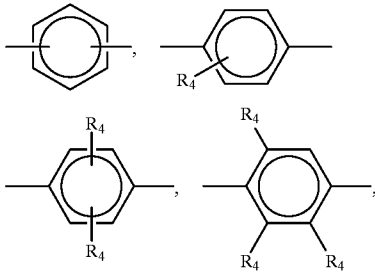
wherein X is a divalent functional group selected from the group consisting of

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and R₄ is CH₃—, Cl—, Br—, F—, or CH₃O— and R₄ can be the same or the different in the case that more than two of them are substituted.

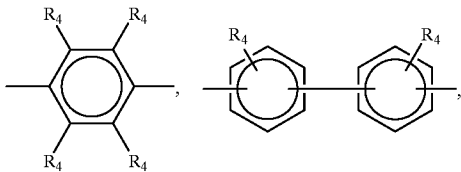
R₂ is a divalent organic group, which has at least one benzene. More concretely, R₂ is at least one selected from group consisting of



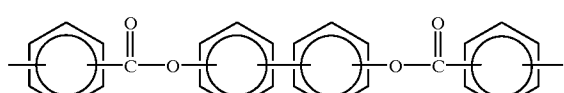
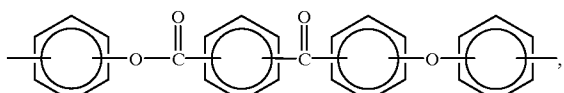
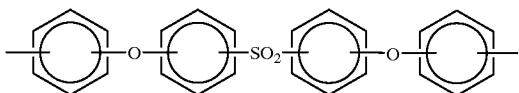
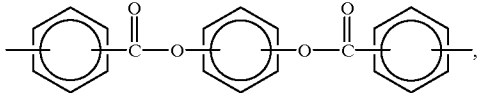
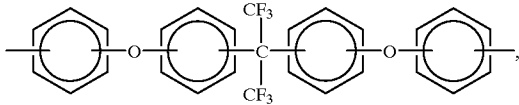
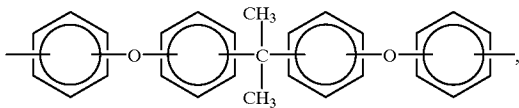
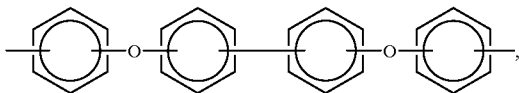
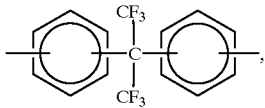
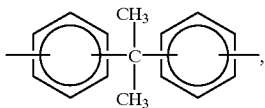
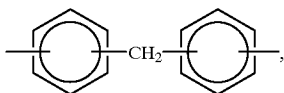
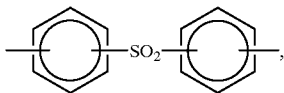
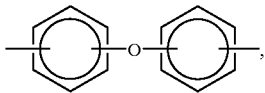
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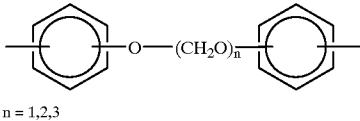
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and

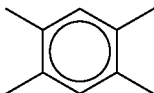
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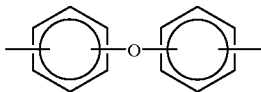
10 wherein R_4 is CH_3- , $\text{Cl}-$, $\text{Br}-$, $\text{F}-$, or $\text{CH}_3\text{O}-$ and R_4 can be the same or different kind in the case that more than two of them are substituted.

15 One of the preferred polyimides contains R_1 represented by



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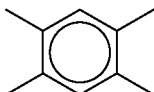
and R_2 represented by



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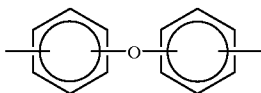
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as the main component respectively. A polyimide copolymer containing R_1 represented by



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and R_2 represented by



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and

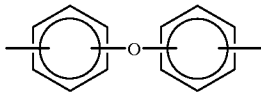


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as the main component respectively is also preferred.

Moreover, it is preferable that the molar ratio of organic group represented by



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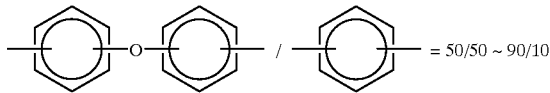
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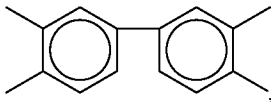
to organic group represented by



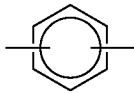
is ranging from 50 to 50 to 90 to 10.



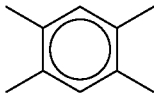
It is also preferable that a polyimide copolymer contains R_1 represented by



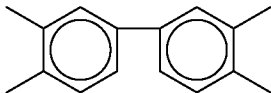
and R_2 represented by



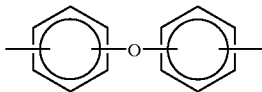
or R_1 represented by



and



and R_2 represented by



and



as the main component respectively.

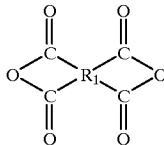
Polyimide resin represented by the above general formula (1) can be obtained by the dehydrating closure reaction of a polyamide acid polymer, which is a precursor of polyimide resin. Polyamide acid solution may be obtained by poly-

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merizing an approximately equal mole of dianhydride and diamine in organic polar solvents according to the conventional method.

One example of the methods for producing polyamide acid is described below. Under an inert atmosphere consisting of, e.g., argon gas, nitrogen gas or the like, at least one kind of acid dianhydrides selected from aromatic tetracarboxylic dianhydrides represented by the general formula (2);

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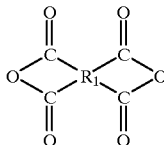
wherein R_1 is a tetravalent organic group, is dissolved or diffused in organic solvents to make a solution. At least one kind of diamine ingredients represented by the general formula (3), wherein R_2 is a bivalent organic group is added to the solution to obtain a polyamide acid polymer. The diamine ingredients can be dissolved or diffused in an organic solvent prior to adding the solution. Alternatively, the diamine in a solid state may be added to the solution. It is preferable that the reacting temperature ranges from -10°C . to 50°C . and the reacting time ranges from 30 minutes to 6 hours.

Alternatively, first, one or more diamines may be dissolved or diffused in an organic solvent to make a solution. Then one or more acetic dianhydrides are added to the solution to obtain a polyimide acid solution. Also, diamines and acetic dianhydrides can be mixed in an organic solution simultaneously.

It is preferable that the average molecular weight of polyimide resin is more than 10,000 in order to maintain the strength of polyimide resin. In many cases, it is difficult to directly measure molecular weight of a polyimide polymer. In such cases, molecular weight is estimated indirectly. For example, in the case that a polyimide polymer is synthesized by polyamide acid, molecular weight of polyimide is considered to be equivalent to that of polyamide acid.

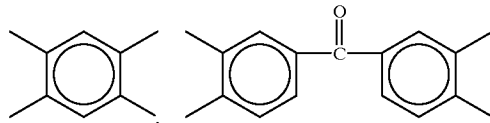
As aromatic tetracarboxylic dianhydride represented by the general formula (2),

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various types of aromatic tetracarboxylic dianhydride can be used. More concretely, in due consideration of balance of various properties, one or more aromatic tetracarboxylic dianhydrides can be selected, wherein R_1 of the general formula (2) is a tetravalent organic group selected from the group consisting of

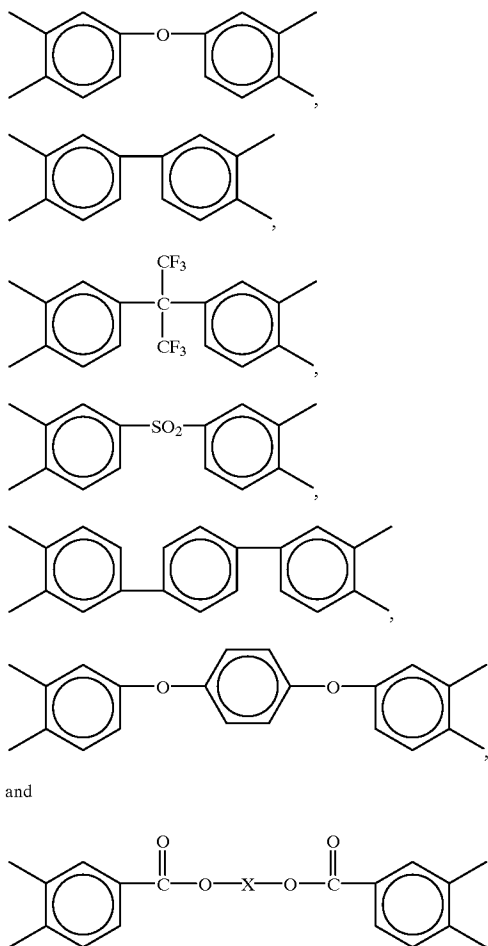
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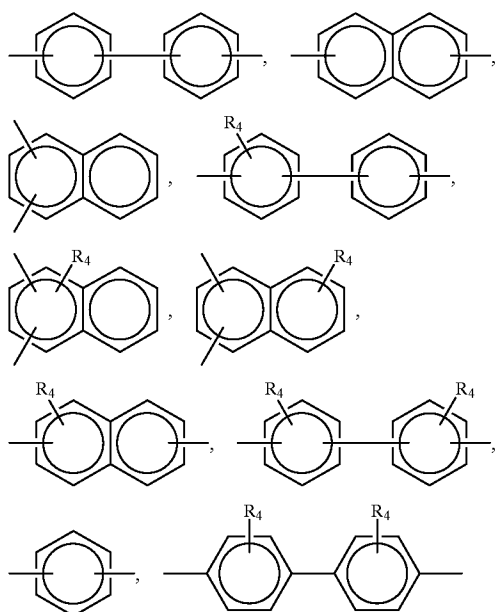
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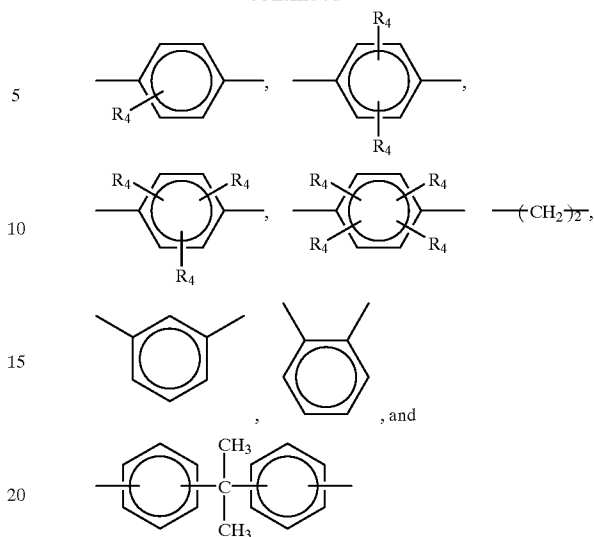


Wherein X is a bivalent functional group represented by



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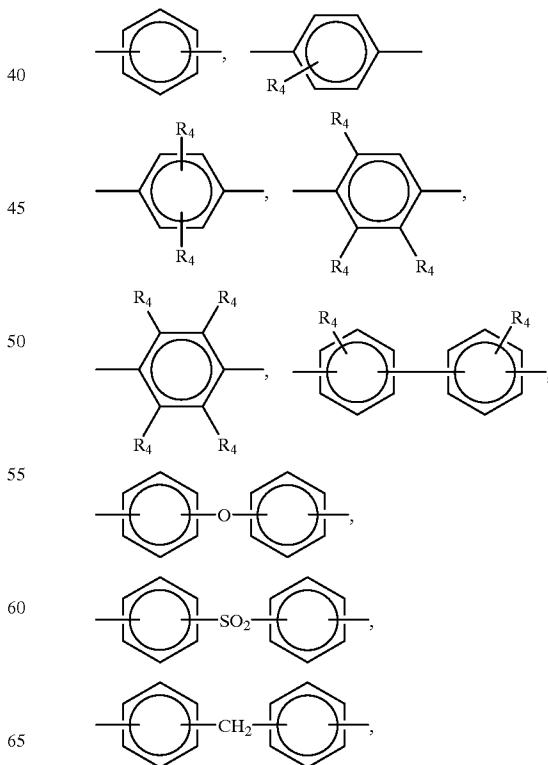


²⁵ R₄ is CH₃—, Cl—, Br—, F—, or CH₃O— and R₄ can be the same or different kind in the case that two or more of them are substituted.

Various types of diamines can be used as a diamine compound represented by the general formula (3).

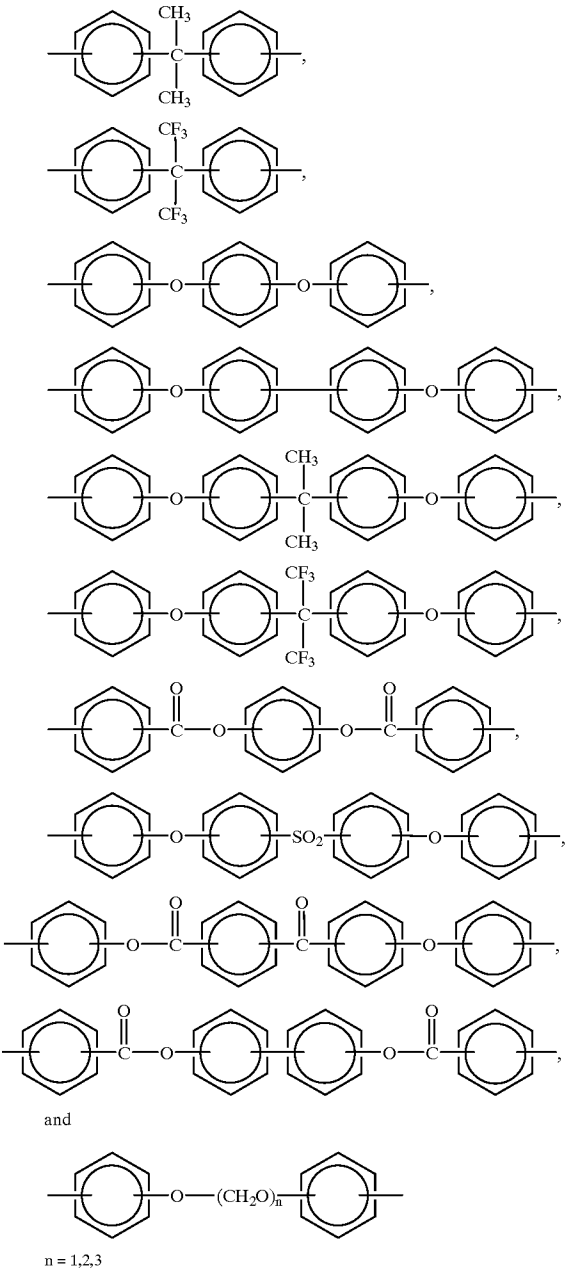


More concretely, in due consideration of balance of various properties, one or more diamines can be selected, wherein R₂ of the general formula (3) is a bivalent organic group selected from the group consisting of



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wherein R_4 is $\text{CH}_3\text{—}$, Cl— , Br— , F— , or $\text{CH}_3\text{O—}$ and R_4 can be the same or different kind in the case that two or more of them are substituted. The examples of organic solvents, which can be used in producing polyamide acid, are as follows: sulfoxide solvents such as dimethylsulfoxide and diethylsulfoxide; formamide solvents such as N,N-dimethylformamide and N,N-diethylformamide; and acetamide solvents such as N,N-dimethylacetamide and N,N-diethylacetamide. One of the above-mentioned organic solvents can be used alone or the combination of two or more of them can be used as mixed organic solvents. Also, the combination of the above polar solvents and inactive solvents of polyamide acid can be used as mixed organic solvents. Examples of such inactive solvents are acetone, methanol, ethanol, isopropanol, benzene, 2-methoxyethanol toluene, xylene, THF and the like.

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Polyimide can be produced from polyamide acid obtained by means of the above-mentioned reaction. Polyimide can be obtained by a chemical-curing method, in which polyamide acid, a precursor of polyimide, is imidated by being heat-treated under the presence of both dehydrating agent represented by acid anhydride including acetic anhydride and tertiary amine including picoline, quinoline, isoquinoline and pyridine. Alternatively, polyimide can be also obtained by means of the heat-curing method, in which imidating reaction proceeds without dehydrating agent and tertiary amine. Since imidating reaction takes place more rapidly in the chemical-curing method, the chemical-curing method can be more productive and profitable than the heat-curing method. Moreover, polyimide obtained from the chemical-curing method has advantages of high mechanical strength and small coefficient of linear expansion.

The use of the chemical-curing method followed by the heat-treating method makes possible speedier imidation. Therefore, it is preferable to produce polyimide film by the combined use of the chemical-curing method and the heat-curing method. In the present invention, said combined use is introduced to the process of imidation.

As shown in FIG. 1, the chemical-curing method is used in the first half of the process and the heat-curing method in the latter half of the process, in which imidation completes. Therefore, "a prefilm" of the present invention is defined as a film obtained after the chemical-curing process but before the heat-curing process.

Next, one example of methods for producing a polyimide film according to the present invention is concretely described below. Typically, the methods for producing a polyimide film by imidating a precursor of polyimide may consist of two processes. The one may be the chemical-curing process executed in the drum or the belt chamber or the equivalent thereof, and the other may be the heat-curing process executed in the tenter chamber or the equivalent thereof.

In the process executed in the belt chamber, a precursor of polyimide mixed by the blender is allowed to flow from the T-die. The precursor of polyimide allowed to flow from the T-die is placed onto the endless belt or on the casting drum to be formed into the shape of film while being hardened. The film-shaped precursor is moved and heated in accordance with the rotation of the belt or the drum while imidation of the film is promoted. In the belt chamber, reaction products which are combustible volatile constituents consisting mainly of acetic acid and organic solvents are transpired.

In the belt chamber, the temperature of atmosphere and rotation speed of the belt or the drum are adjusted for the purpose of prevention of ignition to the combustible volatile constituent transpired from the polyimide resin or to the resin itself. A warm breeze, hot blast, radiant heat, belt heat and the like can be used in the belt chamber.

In the course of the above process, imidation of a film-shaped composition is promoted. After being heated and dried to such an extent that it can support itself, the film-shaped composition is exfoliated from the endless belt to obtain a prefilm.

The inventors of the present invention found out that the amount of volatile constituent and the imidation ratio have a remarkable effect directly on the improvement of an adhesive property of the fished film. Finally, we succeeded in stably providing a film with an excellent adhesive property at a reasonable price by controlling the amount of volatile constituent and the imidation rate of a prefilm within a certain range.

In the case of successive processes, a film-shaped composition is treated in the tenter chamber by using the heat-curing method after being exfoliated from the drum or the belt. This film-shaped composition exfoliated from the drum or the belt can be defined as a prefilm. However, the embodiment of the present invention is by no means limited to the above and various embodiments are applicable. Depending on the situation, an additional heating apparatus including the heat roll can be also applied to the embodiment in order to promote chemical-curing of a film.

In other words, a prefilm can be defined as a film obtained before being put in the tenter chamber or the equivalent thereof in which heat-curing is completed.

In the present invention, the amount of volatile constituent of a prefilm is calculated by using the following formula;

$$\text{volatile constituent (\%)} = \frac{(W - W_0)}{W_0} \times 100$$

W: the weight of a prefilm before being dried
W₀: the weight of a prefilm after being heat-treated at 450° C. for 20 minutes

It is preferable that the amount of volatile constituent of a prefilm exfoliated from a supporter such as the endless belt and the drum should be adjusted to a range of 20–200 weight %. When the amount of volatile constituent of a prefilm is less than 40 weight %, the adhesive strength of a finished polyimide film is improved.

The imidation rate of a prefilm is calculated on the basis of absorbance of a sample prefilm measured by using the method of infrared absorption spectrum. To prepare a sample, a film of about 50 mm in length and about 100 mm in width is cut out of a prefilm and then soaked in methanol solution with 5 weight % of aniline for about an hour. The solution is then changed into methanol and the film is soaked in methanol for about half an hour for three times. Then the film is washed and dried at a room temperature. The absorbance of the sample prepared as such is measured by using the device for Fourier transform infrared absorption spectrum (System 2000, available from Perkin Elmer Co. Ltd.) under the condition of ATM prism KRS-5, a prism entrance angle of 45°, measuring range of 4000 cm⁻¹–4500 cm⁻¹, ten times of measuring and resolution of 4.00. The imidation rate of the sample is calculated by using the following formula;

$$\text{Imidation ratio (\%)} = \frac{n_x}{n_{100}} \times 100$$

n: absorbance of a sample at 1374 cm⁻¹/absorbance of a sample at 1498 cm⁻¹
n_x: n value of a measured film
n₁₀₀: n value of completely (100%) imidated film

Absorbance at 1374 cm⁻¹ is characteristic of an imido group and absorbance at 1498 cm⁻¹ is characteristic of benzene ring. A 100%-imidized film is obtained by forming a composition consisting of a polymer and organic solvent solution identical to the sample into a film shape and then heating the film-shaped composition at 110° C. for 120 seconds, 300° C. for 30 seconds, 450° C. for 70 seconds, 500° C. for 30 seconds and then 500° C. for 5 minutes.

Preferably, the imidation ratio of a prefilm exfoliated from the heated supporter such as the endless belt and the drum is adjusted to 70% or more. An adhesive property of a finished polyimide film is improved by adjusting the imidation ratio in a range of 70% or more. The films made of a prefilm of 70% or more imidation ratio have much higher

adhesive strength than that made of prefilm of less than 70% imidation ratio.

The amount of volatile constituent and the imidation ratio can be adjusted by controlling the temperature and the heating time in the belt chamber. Normally, in the chemical-curing process, heating is executed to promote a reaction. However, in order to exclusively promote chemical-curing rather than heat-curing the temperature is maintained 200° C. or less. It is preferable to gradually raise the temperature of the atmosphere in the belt chamber step by step, so that solvent and reaction product are evaporated. A sudden rise of the temperature causes wrinkles on the film surface due to the difference of the drying speed between the surface and the inside of the film. Also, it causes undesired exfoliation due to partial hardening of the edge.

The temperature in the belt chamber is adjusted depending on the kind and the thickness of a film and the kind of a solvent to be used. The temperature is gradually increased to nearly a boiling point of a solvent. For example, in the case that dimethylformamide is used as a solvent, as a boiling point of dimethylformamide is 153° C., the temperature in the belt chamber is adjusted to 50° C. to 150° C. The highest temperature in the belt chamber has a potent influence on an adhesive property of a finished film. Higher maximum temperature produces a higher adhesive property of a finished film.

Heating time also depends on the thickness of a film, the kind of a film-shaped composition and the highest temperature in the belt chamber. Higher maximum temperature can reduce heating time and production cost.

Next, the belt chamber is concretely described below. The preferable belt chamber is separated into several rooms to differentiate the temperatures between the rooms. In the process shown in FIG. 2, the belt chamber consists of: a parallel stream solidifying room 10, jet stream solidifying rooms 12, an exfoliation room 14. In the room 10, a film cast over the supporter is heated up and then exposed to a gas stream parallel to a film to be solidified to such an extent that the film loses its fluidity. The room 12 consists of one or more sections, in which the film treated in the room 10 is exposed to gas blowing against it to be solidified to such an extent that it can support itself. In the room 14, the film treated in the room 12 is exfoliated from the endless belt 20.

More specifically, a film-shaped composition of polyimide precursor solvent solution from the die 22 is conveyed to the endless belt 20 which may be made from stainless-steel, aluminum-alloy or the like. The pulleys 18 over which the belt 20 is trained contain cooling devices. Then, gas 24 is sent parallel to the surface of the film-shaped composition heated up evenly. The film-shaped composition is gradually solidified by gas 24 to such an extent that a film loses its fluidity in the room 10, while volatile constituent and organic solvents produced in this process are being transpired. The so obtained film-shaped composition is then conveyed to the rooms 12, in which the film-shaped composition is heated by one or several stages, while the jets of gas is blown against the film-shaped composition from nozzles resulting in transpiring volatile constituent and organic solvents. The so treated film-shaped composition, or a prefilm, which is solidified and dried to such an extent that it can support itself is exfoliated from the endless belt 20 in the room 14. This prefilm is heat-treated in the tenter chamber in the next step.

The amount of volatile constituent of the prefilm before heat-treating in the tenter chamber is preferably 40 weight % or less, and more preferably 30 weight % or less in order to improve an adhesive property of a finished film.

Moreover, in the present invention, the imidation ratio of a prefilm is preferably 70% or more, and more preferably 80% or more in order to improve an adhesive property of a finished film.

An adhesive property of a finished polyimide film can be improved by controlling the amount of volatile constituent and the imidation ratio of a prefilm as mentioned above. The amount of volatile constituent and the adhesive strength are correlated, and so are imidation ratio and the adhesive strength. It is presumed that volatile constituent which hinders the adhesive strength of a finished film can be effectively removed by holding down the amount of volatile constituent of a prefilm.

In the next process, the prefilm exfoliated from the endless belt is heat-treated in the tenter chamber with its edges fixed. The tenter chamber can consist of a heating furnace and a device for lowering the temperature gradually. However, it is by no means limited to the above. In the tenter chamber, the film can be moved by shifting a sheet fixed by pins in accordance with rotating drive of a pin conveyer. Imidation of a prefilm is promoted by gradual heat-treatment of the prefilm in the heating furnace, in which heat-curing is executed. Normally, heat-treatment is carried out at the starting temperature of about 200° C. and then the temperature is gradually raised so as to complete imidation of a prefilm. Thus, a finished polyimide film is obtained.

The highest temperature of the heat-treatment is preferably in a range from 450° C. or more to 630° C. or less, and more preferably from 520° C. or more to 580° C. or less. A temperature gradient to the highest temperature can be any form without any special restriction. In the case that the highest temperature is less than 450° C., the adhesive strength of a finished film is not effectively improved. In the case that the highest temperature is more than 630° C., mechanical properties including the adhesive strength is extremely spoiled, which is considered to be caused by heat deterioration of a polyimide film.

As shown in the above embodiment, a prefilm exfoliated from the endless belt can be heat-treated at the highest temperature of 450° C. or more to 630° C. or less successively as the final stage of the whole process. Alternatively, a finished polyimide film produced by the use of the conventional methods can be heat-treated at the temperature of 450° C. or more to 630° C. However, in order to simplify the process and to avoid high production cost, the above heat-treatment is preferred to be carried out in course of producing polyimide.

The heat-treatment can be carried out for few seconds to few minutes, preferably for ten seconds to ten minutes, and more preferably for ten seconds to three minutes, which depends on the heating temperature. For example, heat-treating a polyimide film at 600° C. for ten minutes causes heat deterioration. For another example, heat-treating a polyimide at 500° C. for five seconds does not produce sufficient results on the improvement of an adhesive property.

A polyimide film, which is completely imidized in the above heat-curing process, gradually cooled down in the device for lowering the temperature.

As described above, the method for heat-treating a film at a very high temperature ranging from 450° C. or more to 630° C. or less has never been proposed as a method for improving an adhesive property of a polyimide film in the prior arts. Therefore, the present invention is a novel invention to improve an adhesive property of a finished polyimide film by quite simple heat-treatment. The mechanism is not completely cleared up at the moment, however, an adhesive property is supposed to be improved with the result that a

dense layer is formed on the surface of the film by heat-treating at the high temperature.

A polyimide film obtained by using the method of the present invention includes a sheet-like film with a various thickness ranging from a few micrometers to hundreds of micrometers. The thickness of a film can be selected in accordance with the purpose of use. For example, a film with the thickness of 12.5 μm to 50 μm is used as a base film of a flexible printed wiring board.

The present invention is a method to improve an adhesive property of a finished film by controlling the imidation ratio and the amount of volatile constituent of a prefilm. Moreover, the present invention makes possible to stably and economically provide a film with a higher adhesive property by heat-treating at the high temperature in the tenter chamber.

The present method for producing a polyimide film is described above as an example of the embodiments of the method. However, this invention is by no means limited thereto. As the need arises, other well-known after-treatment such as flame treatment, corona discharge treatment, ultra-violet treatment, alkaline treatment, primer treatment, sand-blast treatment and plasma treatment can be combined with the method of the present invention.

EXAMPLES

The present invention will be more clearly understood by referring to the Examples below. However, the Examples should not be construed to limit the invention in any way. In the Examples, corona discharge treatments were executed against polyimide films at 220±10 W·min/m² of electric power density with the use of aluminum electrode. The adhesive strength of the polyimide film was evaluated by executing the following measuring method: using acrylic adhesive agent "Pyrallux" (a product and trade name of E. I. du Pont de Nemours & Co., Inc.), the polyimide film was laminated with a copper foil having 35 μm of thickness "3EC" (an electrolyzed copper foil, a product of Mitui Metal & Mining Co., Ltd.), and then the above adhesive agent was allowed to react at 185° C. for an hour to be hardened to produce FCCL (flexible copper-clad laminate); a test sample was cut out of the FCCL so that width of copper pattern of the FCCL could become 3 mm, and then the sample was subject to a tension test via 90° of exfoliation at 50 mm/min. of peeling speed by applying a tension tester "S-100-C", a product of Shimazu Seisakusho, Co., Ltd. The results of the average of five measurements are shown in Table 1.

Examples 1~12

The imidation rate and the amount of volatile constituent of a prefilm, and the adhesive strength of a finished product were measured. The heating temperature and time at the stage of chemical curing varied while conditions at the stage of heat-curing were constant.

Polyamide acid solution was prepared from 4,4'-diaminodiphenylether selected from aromatic diamines and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were mixed quickly with the solution. The molar rate of the acetic anhydride to a repeating unit of the polyamide acid was 5.5 to 1, and the molar ratio of the isoquinoline to a repeating unit of the polyamide acid was 0.55 to 1. Then the mixture was formed into a film-shaped composition on the aluminum foil with the thickness of 30 μm. Each film-shaped composition was heated for 30 to 360 seconds at the temperature ranging from 90 to 160° C. in an oven under the

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12 different conditions, and prefilms with the thickness of 25 μm were finally obtained. Then the prefilms were heat-treated at the temperature of 300° C. for 30 seconds and then at the temperature of 500° C. for a minute. Thus the imidation of the prefilms was completed and the finished films were subjected to corona discharge treatment to obtain PI film products.

The amount of volatile constituent and the imidation ratio concerning each prefilm as well as the adhesive strength of each corresponding P1 film product were measured. The results are shown in Table 1.

TABLE 1

	temperature (° C.)	time (sec.)	volatile constituent (%)	imidation ratio (%)	adhesive strength (kg/cm)
Example 1	90	90	216	78	0.79
Example 2	90	180	37	80	1.34
Example 3	90	360	28	80	1.36
Example 4	110	60	256	66	0.79
Example 5	110	90	61	85	1.22
Example 6	110	120	31	87	1.40
Example 7	110	180	25	88	1.43
Example 8	110	240	22	88	1.51
Example 9	160	30	202	80	0.99
Example 10	160	60	25	85	1.54
Example 11	160	90	17	91	1.63
Example 12	160	120	15	94	1.70

Based on the results, the relation between the amount of volatile constituent of prefilms and the adhesive strength of the P1 film products as well as the relation between the imidation ratio of prefilms and the adhesive strength of the P1 film products are shown in FIGS. 3 and 4, respectively.

Table 1 shows that higher temperature in the belt chamber or longer heating time in the case of same temperature makes the amount of volatile constituent decreased and the imidation ratio increased. Table 1, FIG. 3 and FIG. 4 show that less amount of volatile constituent or higher imidation ratio of a prefilm makes the adhesive strength of the finished product increased.

Examples 13~15

Polyamide acid solution was obtained from 4,4'-diaminodiphenylether and para-phenylenediamine selected from aromatic diamines in the molar rate of 3:1 and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were added to the solution. The molar rate of the acetic anhydride to a repeating unit of the polyamide acid was 5.0 to 1, and the molar rate of the isoquinoline to a repeating unit of the polyamide acid was 0.51 to 1. Then the mixture was stirred sufficiently and adjusted to 0° C. to make dope.

The so obtained dope was allowed to flow from a T-die and formed into a film-shaped composition with the thickness of about 250 μm on the smooth metal endless belt consecutively. Then it was dried up by hot air while the belt was rotated. The amount of volatile constituent of three prefilms, each of which was prepared under the conditions that the temperature of the belt chamber was set at 85° C./95° C./100° C., 95° C./105° C./110° C. and 110° C./120° C./125° C. (the total drying time is about 100 seconds), respectively, were measured.

The prefilms exfoliated from the belt were heat-treated at the temperature ranging from 250° C. to 550° C. for about 80 seconds in total in the tenter chamber. Then the films were gradually cooled down to room temperature in the

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cooling room. After that, corona discharge treatment was executed against each film and the adhesive strength of the 25 μm -thick polyimide film obtained under the above three temperature conditions was measured. The results of the measurement are shown in Table 2.

TABLE 2

	volatile constituent (%)	adhesive strength (kg/cm)
Example 13	140	1.2
Example 14	90	1.3
Example 15	40	1.4

Table 2 shows that as the amount of volatile constituent of a prefilm decreases, the adhesive strength of a corresponding film increases.

Examples 16~18

Next, polyimide films were produced under the various conditions of maximum temperature in the heat-curing treatment process in a tenter chamber, while the condition of chemical curing remained constant.

Polyamide acid solution was prepared from 4,4'-diaminodiphenylether selected from aromatic diamines and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were mixed quickly with the solution. The molar ratio of the acetic anhydride to a repeating unit of the polyamide acid was 5.5 to 1, and the molar ratio of the isoquinoline to a repeating unit of the polyamide acid was 0.55 to 1. Then the mixture was formed into a film-shaped composition. After that, the film-shaped composition was heat-treated at the temperature of 120° C. for 100 seconds to obtain a prefilm. Then the prefilm was treated at 270° C. for 30 seconds and at 370° C. for 30 seconds (the temperature was gradually raised). The resulting film was then baked for 30 seconds at the maximum temperature of 500° C., 550° C. and 630° C., respectively. Consequently, three kinds of 25 μm -thick polyimide film were produced under three different conditions.

Examples 19~21

Polyamide acid solution was obtained from 4,4'-diaminodiphenylether and para-phenylenediamine selected from aromatic diamines in the molar ratio of 3:1 and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were mixed quickly with the solution. The molar ratio of the acetic anhydride to a repeating unit of the polyamide acid was 5.0 to 1, and the molar ratio of the isoquinoline to a repeating unit of the polyamide acid was 0.51 to 1. Then the mixture was formed into a film-shaped composition. After that, the film-shaped composition was heat-treated at the temperature of 120° C. for 100 seconds to obtain a prefilm. Then it was heat-treated at 270° C. for 30 seconds and at 370° C. for 30 seconds (the temperature was gradually raised). The resulting film was baked for 30 seconds at the maximum temperature of 500° C., 570° C. and 630° C., respectively. Consequently, three kinds of 25 μm -thick polyimide films were produced under three different conditions.

The adhesive strength of each 25 m-thick polyimide film obtained in Example 16 to 21 was evaluated. The results are shown in Table 3.

TABLE 3

	maximum temperature (° C.)	time (sec.)	adhesive strength (kg/cm)
Example 16	500	30	0.6
Example 17	550	30	0.7
Example 18	630	30	0.7
Example 19	500	30	0.6
Example 20	570	30	0.8
Example 21	630	30	0.8

Table 3 shows that the higher maximum temperature produces higher adhesive strength.

A polyimide films which were heat-treated at the various temperatures under the equal maximum condition of 450° C. were compared as follows.

Example 22

Polyamide acid solution was prepared from 4,4'-diaminodiphenylether selected from aromatic diamines and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were mixed quickly with the solution. The molar ratio of the acetic anhydride to a repeating unit of the polyamide acid was 5.5 to 1, and the molar ratio of the isoquinoline to a repeating unit of the polyamide acid was 0.55 to 1. Then the mixture was formed into a film-shaped composition. After that, the film-shaped composition was heat-treated at the temperature of 120° C. for 100 seconds to obtain a prefilm. Then it was heat-treated at 270° C. for 30 seconds and at 370° C. for 30 seconds (the temperature was gradually raised). The resulting film-shaped composition was then baked for a minute at the maximum temperature of 450° C. Consequently, 25 μm-thick polyimide film was produced.

Example 23

Polyamide acid solution was obtained from 4,4'-diaminodiphenylether and para-phenylenediamine selected from aromatic diamines in the molar ratio of 3:1 and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were mixed quickly with the solution. The molar ratio of the acetic anhydride to a repeating unit of the polyamide acid was 5.0 to 1, and the molar ratio of the isoquinoline to a repeating unit of the polyamide acid was 0.51 to 1. Then the mixture was formed into a film-shaped composition. After that, the film-shaped composition was heat-treated at the temperature of 120° C. for 100 seconds to obtain a prefilm. Then it was heat-treated at 270° C. for 30 seconds and at 370° C. for 30 seconds (the temperature was gradually raised). The resulting film-shaped composition was then baked for a minute at the maximum temperature of 450° C. Consequently, a 25 μm-thick polyimide film was produced.

The adhesive strength of a 25 μm-thick polyimide film obtained in Example 22 to 23 was measured. The results are shown in Table 4.

TABLE 4

	maximum temperature (° C.)	time (min.)	adhesive strength (kg/cm)
Example 22	450	5	0.3
Example 23	450	5	0.3

These results show that the adhesive strength of the film heat-treated at a low maximum temperature is lower than that of the film heat-treated at a high maximum temperature.

Examples 24~25

Polyimide films obtained in the Examples 22 and 23 were heat-treated at the temperature of 550° C. and 570° C. which were equal condition of the Examples 17 and 20, and then the adhesive strength of each film was measured. The results are shown in Table 5.

TABLE 5

additional treatment		adhesive strength (kg/cm)
Example 24	Example 22 + 550° C. × 30 sec.	0.7
Example 25	Example 23 + 570° C. × 30 sec.	0.8

These results show that the adhesive strength of a polyimide film obtained in the Example 22 or 23 was provided with as high adhesive strength as that of a film obtained in the Example 17 or 20.

Examples 26~28

Polyamide acid solution was obtained from 4,4'-diaminodiphenylether and para-phenylenediamine selected from aromatic diamines in the molar ratio of 3:1 and pyromellitic acid dianhydride selected from aromatic tetracarboxylic dianhydrides. Acetic anhydride and isoquinoline were added to the solution. The molar ratio of the acetic anhydride to a repeating unit of the polyamide acid was 5.8 to 1, and the molar ratio of the isoquinoline to a repeating unit of the polyamide acid was 0.59 to 1. Then the mixture was stirred sufficiently and adjusted to 0° C. to make dope.

The so obtained dope was allowed to flow from a T-die and formed into a film-shaped composition with the thickness of about 250 μm on the smooth metal endless belt consecutively. Then it was dried up by hot air while the belt was rotated. The temperature conditions of the belt chamber was set at 110° C./120° C./125° C. and the total drying time was about 100 seconds.

The prefilms exfoliated from the endless belt were heat-treated in the tenter chamber at the temperature starting from 250° C. up to 500° C., 530° C., or 560° C. (gradually heated up) for about 80 seconds in total. Then the films were gradually cooled down to room temperature in the cooling room. After that, corona discharge treatment was executed against each film and the adhesive strength of the 25 μm-thick polyimide film obtained under the above three temperature conditions was measured. The results of the measurement are shown in Table 6.

TABLE 6

	maximum temperature (° C.)	adhesive strength (kg/cm)
Example 26	500	1.3
Example 27	530	1.4
Example 28	560	1.5

These results show that higher maximum temperature produces higher adhesive strength.

In this way, inventors of the present invention pay their attention to the relation between the amount of volatile constituent of a prefilm or the imidation ratio and the adhesive property of a finished film, and the relation between temperature condition of heat-treating of the prefilm and the adhesive property, to which no attention has been given so far.

This invention makes it possible to enhance the adhesive strength of a finished polyimide film by controlling the amount of volatile constituent and the imidation ratio of a prefilm; the temperature and time of heat-treating; and the maximum temperature in a heat-curing process.

Having now fully described the invention, it will be apparent to one of ordinary skills in the art that various changing and modifications can be made thereto without departing from the spirit or scope of the present invention as set forth herein.

What is claimed is:

1. A method for producing an adhesive polyimide film comprising:

casting a composition into a film shape, wherein said composition consists substantially of an organic solvent solution of polyamide acid and chemical curing agents selected from the group consisting of dehydrating agents and tertiary amines;

heating the film shaped composition at an initial temperature of 200° C. or less, and thereafter increasing the temperature in a step-wise fashion such that solvent is evaporated to form a chemically cured prefilm while adjusting an imidation ratio represented by the formula:

$$\frac{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) \text{prefilm}}{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) 100 \% \text{ imidated film}}$$

and

further heating said prefilm to obtain an adhesive polyimide film.

2. A method for producing an adhesive polyimide film comprising:

casting a composition into a film shape, wherein said composition consists substantially of an organic solvent solution of polyamide acid and one or more chemical curing agents selected from the group consisting of a dehydrating agent and a tertiary amine;

heating the film shaped composition at an initial temperature of 200° C. or less, and thereafter increasing the temperature in a step-wise fashion such that solvent is evaporated to form a chemically cured prefilm while adjusting amounts of volatile constituent; and

further heating said prefilm to obtain an adhesive polyimide film.

3. A method for producing an adhesive polyimide film comprising:

casting a composition into a film shape, wherein said composition consists substantially of an organic solvent solution of polyamide acid and chemical curing agents selected from the group consisting of dehydrating agents and tertiary amines;

heating the film shaped composition at an initial temperature of 200° C. or less, and thereafter increasing the temperature in a step-wise fashion such that solvent is evaporated to form a chemically cured prefilm while adjusting amounts of organic solvent and an imidation ratio represented by the formula:

$$\frac{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) \text{prefilm}}{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) 100 \% \text{ imidated film}}$$

and

further heating said prefilm to obtain an adhesive polyimide film.

4. A method for producing a polyimide film according to claim 1 or claim 3, wherein said adjusted imidation ratio of the prefilm is 70% or more.

5. A method for producing a polyimide film according to claim 2 or claim 3, wherein said adjusted amount of volatile constituent of the prefilm is 40 weight % or less.

6. A method for producing a polyimide film according to claim 3, wherein said adjusted imidation ratio of the prefilm is 70% or more and said adjusted amount of volatile constituent of the prefilm is 40 weight % or less.

7. A method for producing a polyimide film according to any of claims 1, 2 or 3, wherein the highest temperature of heating a prefilm is in a range from 450° C. to 630° C.

8. A method for controlling adhesiveness of a polyimide film comprising:

casting a composition into a film shape, wherein said composition consists substantially of an organic solvent solution of polyamide acid and chemical curing agents selected from the group consisting of dehydrating agents and tertiary amines;

heating the film shaped composition at an initial temperature of 200° C. or less, and thereafter increasing the temperature in a step-wise fashion such that solvent is evaporated to form a chemically cured prefilm while adjusting an imidation ratio represented by the formula:

$$\frac{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) \text{prefilm}}{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) 100 \% \text{ imidated film}}$$

and
further heating said prefilm to obtain an adhesive polyimide film.
9. A method for controlling adhesiveness of a polyimide film comprising:
casting a composition into a film shape, wherein said composition consists substantially of an organic solvent solution of polyamide acid and one or more chemical curing agents selected from the group consisting of a dehydrating agent and a tertiary amine;
heating the film shaped composition at an initial temperature of 200° C. or less, and thereafter increasing the temperature in a step-wise fashion such that solvent is evaporated to form a chemically cured prefilm while adjusting amounts of volatile constituent; and
further heating said prefilm to obtain an adhesive polyimide film.
10. A method for controlling adhesiveness of a polyimide film comprising:
casting a composition into a film shape, wherein said composition consists substantially of an organic solvent solution of polyamide acid and chemical curing agents selected from the group consisting of dehydrating agents and tertiary amines;

heating the film shaped composition at an initial temperature of 200° C. or less, and thereafter increasing the temperature in a step-wise fashion such that solvent is evaporated to form a chemically cured prefilm while adjusting amounts of organic solvent and an imidation ratio represented by the formula:

$$\frac{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) \text{prefilm}}{\left(\frac{\text{imido group infrared absorbance at } 1374 \text{ cm}^{-1}}{\text{benzene ring infrared absorbance at } 1498 \text{ cm}^{-1}} \right) 100 \% \text{ imidated film}}$$

and
further heating said prefilm to obtain an adhesive polyimide film.
11. The method according to claim 8 or claim 10, wherein the adjusted imidation ratio of the prefilm is 70% or more.
12. The method according to claim 9 or claim 10, wherein the adjusted amount of volatile constituent of the prefilm is 40 weight % or less.
13. The method according to claim 10, wherein the adjusted imidation ratio of the prefilm is 70% or more and the adjusted amount of volatile constituent of the prefilm is 40 weight % or less.
14. The method according to any one of claims 8-10, wherein the highest temperature for heating a prefilm is in a range from 450° C. to 630° C.

* * * * *

EXHIBIT E

(12) **United States Patent**
Yabuta et al.

(10) **Patent No.: US 6,746,639 B2**
(45) **Date of Patent: Jun. 8, 2004**

(54) **PROCESS FOR PREPARING POLYIMIDE FILM**

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(52) **U.S. Cl.** **264/176.1**; 264/177.17;
264/211.12; 264/216
(58) **Field of Search** 264/176.1, 177.17,
264/211.12, 216

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(57) **ABSTRACT**

There is provided a process for preparing a polyimide film by a method of casting a film, wherein bubble inclusion and unevenness in thickness are prevented without decrease in mechanical strength at the same time. It is an object of the present invention to provided a process for preparing a polyimide film characterized by extruding, casting and forming into a film a composition of a resin solution obtained by adding, to low viscosity varnish obtained by polymerizing a tetracarboxylic dianhydride component with a diamine component in a molar ratio of 1:1.01 to 1:1.05, or 1:0.95 to 1:0.99, a dehydrating agent in a molar ratio of at least one time and a chemically-imidizing catalyst in a molar ratio of at least half time based on 1 mole of the amic acid of the poly(amic acid) varnish.

6 Claims, 1 Drawing Sheet

FIG. 1

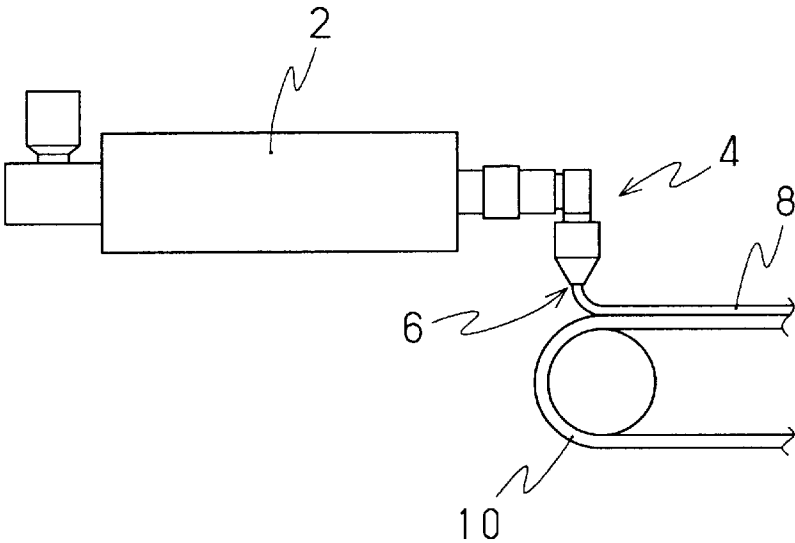
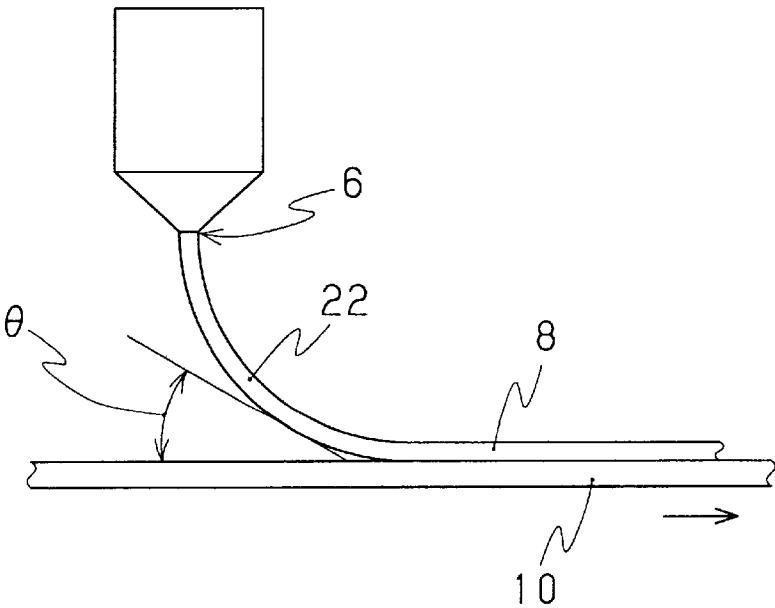


FIG. 2



PROCESS FOR PREPARING POLYIMIDE FILM

BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing a polyimide film by a casting process with a T-die in extrusion. Specifically, the present invention relates to a process for preparing a polyimide film, wherein bubbles are prevented from being mixed into a resin solution (referred to as "curtain" in the present specification) which is extruded from a die in a T-die method, and unevenness in thickness is controlled, and wherein mechanical properties, especially tensile strength, of the polyimide film to be obtained are prevented from decreasing.

Among plastic materials, polyimides have excellent properties in heat resistance, insulating properties, solvent resistance and low temperature resistance, and are used as a material for electrical and electronic parts. Specifically, they are used for flexible print circuit, base films in TAB carrier tape, coating materials of electric cables for aircraft and the like, base films in magnetic recording tape, coating materials of superconducting coil wire, and the like. A polyimide film suitable for each purpose is selected appropriately for the above various purposes.

In accordance with miniaturization and thin filming in electrical and electronic parts, line thinning of circuit is in progress. Dimensional change of materials during use may cause accidents such as disconnection and short-circuit in thinly lined circuit structure. Therefore, highly accurate dimensional stability is required for materials used for electrical and electronic parts.

Meanwhile, as shown in FIG. 1, a polyimide film is prepared as follows. A polyimide precursor, i.e., a composition of poly(amic acid) solution is mixed with a chemically-imidizing catalyst in an extrusion machine 2; the mixture is spread from the extrusion machine 2 in the cross direction; and then the mixture is extruded continuously into a smooth, thin film through a die lip 6, namely, a narrow slit space set on a slit die 4 on an endless belt 10. Then, in the progress of imidizing the above composition of poly(amic acid) solution, a resin film 8 is hardened by drying and cooling to such a degree that the resin achieves self supportability; and further, the hardened resin is heat-treated to prepare a polyimide film.

However, in the above process for preparing a polyimide film, an acid dianhydride component and a diamine component are normally mixed in almost equimolar amount, specifically in a component ratio ranging from about 1:0.095 to 1:1.005 as raw materials of a poly(amic acid) composition to obtain the poly(amic acid) composition. The poly(amic acid) composition is usually a viscous liquid whose viscosity is adjusted to at least 2,500 poise. The viscosity of a liquid or slurry composition of a resin solution is usually in the range of 500 to 2,000 poise when it is extruded from the slit die after mixing the above poly(amic acid) composition and the chemically-imidizing agent.

Also, a polyimide film is obtained by casting a poly(amic acid) composition which is a polyimide precursor according to a casting method with a T-die. Thereafter, imidization is completed through film forming, heating and drying, to obtain a polyimide film. During the casting step, if imidizing reaction of the poly(amic acid) composition proceeds rapidly, a resin film is partially imidized, leading to problems with generation of gel defect parts in a film as well as formation of coating streaks since the slit die is clogged with

the gel generated by the partial imidization of the poly(amic acid) composition. Therefore, in order to control the imidizing reaction of the poly(amic acid) composition, the composition of poly(amic acid) solution is generally cooled to at most 0° C. Viscosity of the composition of poly(amic acid) solution tends to become considerably high due to the cooling.

A composition of a resin solution has elasticity when it has a relatively high viscosity such as the above, namely, 500 to 2,000 poise. Therefore, as shown in FIG. 2, curtain 22 which is a fluid composition of a resin solution extruded from the die lip 6 is drawn to machine direction as the speed of an endless belt 210 accelerates. Once the curtain 22 is drawn to the machine direction, an angle θ formed when the curtain 22 reaches the endless belt 10 becomes smaller. Accordingly, when the curtain 22 reaches the surface of the endless belt 10, air is easily included between the curtain 22 and the endless belt.

As a result, air can be included between the prepared resin film 8 and the endless belt 10, and foamed projection parts having large and small sizes may remain on the surface of the resin film 8. The inclusion of bubbles causes to deteriorate surface properties of resin film remarkably. For example, in the drying step of the above resin film, the film thickness of the projected part becomes thin, the included air is expanded to break some part of the resin film, and defective parts are generated.

Further, since the above-mentioned high viscosity curtain has stronger elasticity and larger adhesive strength to the belt than low viscosity curtain, it is drawn to the machine direction depending on the movement of the belt. However, when the curtain is drawn to the machine direction for at least a certain distance, the reaching point of curtain varies periodically since reverse force is generated against the machine direction due to the elasticity of the resin film. The periodic variance causes variation in thickness of the resin film to be prepared, and therefore periodic unevenness in thickness is generated in the machine direction, resulting in the problem that such unevenness appears as striping on the surface of the film as the final product.

In response to this problem, Japanese Unexamined Patent Publication 198157/1999 discloses a process for casting a film in which viscosity of a composition of a resin solution in a die is lowered. The process aims at preventing bubble inclusion at casting a resin film, improving uneven thickness and promoting production efficiency of the film even in a process for casting a film at high speed. As a process for lowering viscosity of a composition of a resin solution in a die, there are disclosed a process for decreasing polymerization degree of a composition of a resin solution and a process for increasing the ratio of the solvent in the composition of a resin solution.

However, a polyimide film prepared according to the process for lowering the polymerization degree disclosed in Japanese Unexamined Patent Publication 198157/1999 had a problem that mechanical properties of the film are significantly reduced compared with a polyimide film prepared from equimolar diamine component and tetracarboxylic dianhydride component. Also, in the process for increasing the ratio of the solvent in the composition of a resin solution disclosed in Japanese Unexamined Patent Publication 198157/1999, temperature of the belt needs to be raised high in order to dry the resin on the endless belt to such a degree that self supportability is achieved, and in consequence, mechanical properties of the polyimide film to be obtained is lowered.

As mentioned above, in the process for casting a film in which inclusion of bubbles are prevented at casting a resin film and uneven thickness is improved, there is a problem that mechanical properties of the polyimide film to be obtained are lowered significantly. The lowering of the mechanical properties causes to disturb stable production due to generation of waviness made by film extension in the process of producing flexible printcircuit, base films in TAB carrier tape, coating materials of electric cables for aircraft and the like, base films in magnetic recording tape, coating materials of superconducting coil wire, and the like. Also, mechanical properties of products made therefrom are lowered even to make the products unreliable.

SUMMARY OF THE INVENTION

The present invention is to provide a process for preparing a polyimide film wherein inclusion of bubbles are prevented at resin film casting, and uneven thickness is improved especially in such a cast film forming process for preparing polyimide film at high speed as the above without the lowering of mechanical properties as seen in the process for casting a film disclosed in Japanese Unexamined Patent Publication 198157/1999 at the same time.

The present invention has been carried out to solve the above problems. The process for preparing a polyimide film of the present invention relates to a process for preparing a polyimide film by extruding and casting a composition of a resin solution containing a poly(amic acid) varnish, which comprises a step for preparing the poly(amic acid) varnish which is a varnish having low viscosity by polymerizing a tetracarboxylic dianhydride component with a diamine component in a molar ratio of 1:1.01 to 1:1.05, or 1:0.95 to 1:0.99, and a step for preparing the composition of a resin solution by adding, to the poly(amic acid) varnish, a dehydrating agent in a molar ratio of at least 1 time and a chemically-imidizing catalyst in a molar ratio of at least half time based on 1 mole of the amic acid of the poly(amic acid) varnish.

It is preferable that viscosity of the poly(amic acid) varnish is at most 2,000 poise at 20° C.

It is also preferable that viscosity of the poly(amic acid) varnish is at most 1,500 poise at 20° C.

It is preferable that viscosity of the poly(amic acid) varnish is 100 to 1,500 poise at 20° C.

It is preferable that the composition of a resin solution is obtained by adding the dehydrating agent of at least 1.2 to 5 times and the chemically-imidizing catalyst of at least 0.6 to 2.0 times in molar ratio based on 1 mole of the amic acid of the poly(amic acid) varnish.

It is preferable that the chemically-imidizing catalyst is a tertiary amine.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a view showing a process for preparing a polyimide film.

FIG. 2 is a view showing the state of curtain extruding from a die lip according to a process for casting a film.

DETAILED DESCRIPTION

Embodiments of the process for preparing polyimide film of the present invention are explained below. "Curtain" in this specification means a fluid composition of a resin solution shaped like a curtain which exists in air gap space between a slit die from which the composition is extruded and a belt which the composition reaches.

The process for preparing polyimide film of the present invention is as follows. A tetracarboxylic dianhydride component is mixed with a diamine component, and a composition of a resin solution containing a poly(amic acid) varnish comprising a poly(amic acid) is prepared by polymerization of the above two components. While the above composition of a resin solution is extruded, cast and film-formed, the poly(amic acid) is imidized to prepare a polyimide film.

Herein, the present invention is characterized in that the process includes a step for preparing low viscosity poly(amic acid) varnish by polymerizing a tetracarboxylic dianhydride component and a diamine component by arranging the component ratio to a specific range.

The imidizing reaction of the poly(amic acid) obtained in the above method is carried out by a chemical method to add a dehydrating agent and a chemically-imidizing catalyst to the poly(amic acid) varnish. Another characteristic of the present invention is that a composition of a resin solution is prepared by adding the dehydrating agent and the chemically-imidizing agent used for the imidization of the poly(amic acid) in a specific ratio. By extruding, casting and film-forming this composition of a resin solution, it is possible to obtain a polyimide film whose mechanical properties are not lowered, inclusion of bubbles being prevented at the casting of a resin film and uneven thickness being improved.

Hereinafter, embodiments of the process for preparing a polyimide film is specifically explained.

The ratio of the tetracarboxylic dianhydride component and the diamine component which are the raw materials of poly(amic acid) is in the range of 1:1.01 to 1:1.05 or 1:0.95 to 1:0.99 in molar ratio. The above molar ratio is preferably in the range of 1:1.01 to 1:1.03 or 1:0.97 to 1:0.99. When diamine component is less than 1.01 mole approaching 1.00 mole based on 1 mole of the tetracarboxylic dianhydride component, viscosity of poly(amic acid) varnish to be obtained becomes higher. In this case, it is impossible to obtain an excellent polyimide film because the intact varnish causes to include bubbles at casting a resin film and to generate uneven thickness. Then, even though the high viscosity varnish is diluted by a solvent, the ratio of the solvent in the low viscosity varnish to be obtained is increased. Therefore, in order to dry the above varnish on the endless belt to such a degree that it achieves self supportability, temperature of the belt needs to be raised, resulting in remarkable decrease in mechanical properties of the polyimide film to be obtained. Specifically, tensile strength of the polyimide film obtained by dilution is lower than 90% of that of the polyimide film prepared from poly(amic acid) varnish which is not diluted.

Also, as to the component ratio of the tetracarboxylic dianhydride component and the diamine component, when the diamine component is more than 1.05 mole or less than 0.95 mole based on 1 mole of the tetracarboxylic dianhydride component, polymerization degree of the poly(amic acid) varnish to be obtained is low, resulting in remarkable decrease in mechanical properties of the polyimide film to be obtained. Specifically, tensile strength of the polyimide film to be obtained is lower than 90% of that of the polyimide film prepared by a usual non-fast casting method in which poly(amic acid) varnish is prepared by polymerizing a tetracarboxylic dianhydride component and a diamine component in an almost equimolar ratio, specifically, in a molar ratio of 1:1 to 1:1.005 or 1:0.995.

Any known polymerization method can be used, but the following methods are particularly preferable. That is, (1) a

method of polymerization in which aromatic diamine dissolved in an organic polar solvent is allowed to react with aromatic tetracarboxylic dianhydride in an amount substantially equimolar therewith; (2) a method of polymerization in which aromatic tetracarboxylic dianhydride is allowed to react with an aromatic diamine compound in an organic polar solvent in an amount under-molar therewith to obtain a pre-polymer having a dianhydride group at both ends, and in which polymerization is performed using an aromatic diamine compound so that amounts of aromatic tetracarboxylic dianhydride and the aromatic diamine compound can be substantially equimolar in whole processes; (3) a method of polymerization in which aromatic tetracarboxylic dianhydride is allowed to react with an aromatic diamine compound in an organic polar solvent in an amount excess-molar therewith to obtain a pre-polymer having an amino group at both ends, and in which an additional aromatic diamine compound is added thereto and polymerization is preformed using aromatic tetracarboxylic dianhydride so that amounts of aromatic tetracarboxylic dianhydride and the aromatic diamine compound can be substantially equimolar in whole processes; (4) a method of polymerization in which aromatic tetracarboxylic dianhydride is dissolved and/or dispersed in an organic polar solvent and then polymerization is performed using an aromatic diamine compound so that the amounts can be substantially equimolar; (5) a method of polymerization in which a mixture of aromatic tetracarboxylic dianhydride and aromatic diamine in substantially equimolar amounts is allowed to react in an organic polar solvent; and the like.

Any method can be used as long as a molar ratio between dianhydride and a diamine compound is in the range of 1:1.01 to 1:1.05, or 1:0.95 to 1:0.99.

Basically, the poly(amic acid) varnish is obtained by polymerizing, in an organic polar solvent, aromatic tetracarboxylic dianhydride represented by pyromellitic dianhydride with aromatic diamine represented by 4,4'-diaminodiphenyl ether and paraphenylenediamine in the state of uniform dissolution in the above organic polar solvent. The method of polymerizing a tetracarboxylic dianhydride component with a diamine component is not particularly limited, and the polymerization can be conducted by any known method. For example, one or two kinds of diamine are dispersed in an organic solvent in the state of solution or slurry under inert gas such as argon or nitrogen. To the solution is added at least one of tetracarboxylic dianhydride in the state of solid, solution with an organic solvent or slurry to obtain poly(amic acid) varnish. In this case, the reaction temperature is preferably -20° C. to 50° C., more preferably at most 20° C. The reaction time is preferably one to two hours.

On the contrary, tetracarboxylic dianhydride may be dissolved or dispersed in an organic solvent at first, and then diamine in the state of solid, solution with an organic solvent or slurry may be added to the solution. Also, the two components can be added at the same time. The order of adding the tetracarboxylic dianhydride component and the diamine component is not limited.

Examples of the aromatic tetracarboxylic dianhydride component are pyromellitic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 2,2',3,3'-biphenyl tetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, oxydiphthalic dianhydride; aromatic diester tetracarboxylic dianhydride such as 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride,

p-phenylene bis(trimellitic acid monoesteracid dianhydride), 1,4-naphthalene bis(trimellitic acid monoesteracid dianhydride), 2,6-naphthalene bis(trimellitic acid monoesteracid dianhydride), and 4,4-biphenylene bis(trimellitic acid monoesteracid dianhydride); and the like. These can be used alone or in combination of two or more. Also, examples of the aliphatic tetracarboxylic dianhydride are 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic dianhydride, 1,2,4,5-cyclohexanetetracarboxylic dianhydride, 2,3,5-tricarboxycyclopentyl acetic acid dianhydride, 3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalene succinic acid dianhydride, and the like. These can be used alone or in combination of two or more. Among these, pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, and p-phenylene bis(trimellitic acid monoesteracid dianhydride) are preferable from the viewpoint of heat resistance, mechanical strength, dimension stability, resistant property at low temperature in the composition of poly(amic acid) as a precursor of polyimide used in the present invention.

Examples of the aromatic diamine component are 4,4'-diaminodiphenyl ether, paraphenylenediamine, metaphenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfide, 3,3'-dimethyl-4,4'-diaminobiphenyl, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 4,4'-bis(4-aminophenoxy)biphenyl, 3,3'-dimethoxybenzidine, diaminonaphthalene, and the like. These can be used alone or in combination of two or more.

Examples of the aliphatic diamine are bis(4-aminocyclohexyl)methane, bis(4-amin-3-methylcyclohexyl)methane, tetramethylene diamine, hexamethylene diamine, diaminosiloxane, and the like. These can be used alone or in combination of two or more. Among these, 4,4'-diaminodiphenyl ether and paraphenylenediamine are preferable from the viewpoint of heat resistance, mechanical strength, dimension stability, resistant property at low temperature. A mixture, which is obtained by mixing these two diamines in an amount of 100:0 to 0:100, preferably 100:0 to 10:90, can be preferably used.

Examples of the organic polar solvent used for the polymerization of the poly(amic acid) are sulfoxide solvents such as diaminoethyl sulfoxide, formamide solvents such as N,N-dimethylformamide, acetoamide solvents such as N,N-dimethylacetoamide, pyrrolidone solvents, phenol solvents and the like. These organic polar solvents can be used alone, as a mixed solvent comprising at least two of these, or further by mixing aromatic hydrocarbon. Among these, N,N-dimethylformamide and N,N-dimethylacetoamide are preferable.

The concentration of solid material of the poly(amic acid) in the above poly(amic acid) varnish is preferably 12.5 to 30% by weight, more preferably 15 to 25% by weight, most preferably 15 to 20% by weight. When the concentration of the solid material of the poly(amic acid) in the varnish is less than 12.5% by weight, temperature of the belt needs to be raised to dry the varnish on the endless belt so that it achieves self supportability, resulting in a tendency that mechanical properties of the polyimide film to be obtained are remarkably decreased. Specifically, tensile strength of the polyimide film obtained in this case is lower than 90% of that of the polyimide film prepared by a usual non-fast casting method in which poly(amic acid) varnish is prepared by polymerizing a tetracarboxylic dianhydride component

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and a diamine component in an almost equimolar ratio, specifically, in a molar ratio of 1:1 to 1.005 or 1:1 to 0.995. On the other hand, when the concentration of the solid material of the poly(amic acid) in the varnish is more than 30% by weight, required low viscosity varnish cannot be obtained, resulting in tendencies that film thickness unevenness in the machine direction remarkably increases and that bubble inclusion occurs easily.

Herein, viscosity of the poly(amic acid) varnish obtained by polymerizing a tetracarboxylic dianhydride component and a diamine component in a molar ratio adjusted to 1:1.01 to 1:1.05 or 1:0.95 to 1:0.99 is preferably at most 2,000 poise, more preferably at most 1,500 poise, most preferably 100 to 1,500 poise at 20° C. Polymerization degree of the poly(amic acid) obtained by polymerization in this adjusted range is relatively low. When viscosity is more than 2,000 poise, there is a tendency that film thickness unevenness in the machine direction remarkably increases, and it is not preferable since bubble inclusion into the resin film occurs easily. On the other hand, when viscosity is less than 100 poise, stability of curtain extruded from a die cannot be maintained and stable film forming becomes difficult in the casting process with a die of the present invention. These viscosity values are measured by a Brookfield type viscometer.

Viscosity of the above poly(amic acid) varnish is adjusted by controlling polymerization degree of an acid dianhydride component and a diamine component which are materials of the poly(amic acid) to a specific molar ratio and by regulating concentration of solid content.

In the next place, a film is formed by chemical imidization of the above poly(amic acid) into polyimide. The chemical imidization means to add a chemically-imidizing agent comprising a dehydrating agent and a chemically-imidizing catalyst to the poly(amic acid). In the present invention, a composition of a resin solution is prepared by adding a dehydrating agent in a molar ratio of at least one time and a chemically-imidizing catalyst in a molar ratio of at least half time based on 1 mole of the amic acid of the poly(amic acid) varnish. To the poly(amic acid) are added the dehydrating agent of preferably at least 1.2 to 5 times, more preferably 1.0 to 4 times, particularly 1.2 to 3 times and the chemically-imidizing catalyst of preferably at least 0.6 to 2.0 times, more preferably 0.5 to 1.5 times, particularly 0.5 to 1.2 times in molar ratio based on 1 mole of the amic acid of the poly(amic acid) varnish. If the amount of the dehydrating agent is out of this range, mechanical properties of the film tend to decrease. If the amount of the chemically-imidizing catalyst is less than this amount, mechanical properties of the film tend to decrease. If the amount is more than this amount, chemical imidizing reaction suddenly proceeds and it becomes impossible to cast it from a die. Examples of the dehydrating agent to be used are organic carboxylic anhydrides, N,N'-dialkylcarbodiimides, lower fatty acid halides, halogenated lower fatty acid anhydride, arylphosphonic acid dihalide and thionyl halide. Among these, organic carboxylic anhydrides are preferable.

Examples of the organic carboxylic anhydrides are acetic anhydride, propionic anhydride, butyric anhydride, valeric anhydride, and the mixture of intermolecular anhydride and organic carboxylic anhydride thereof. Also, examples are carboxylic acid anhydrides of aromatic monocarboxylic acid such as benzoic acid or naphthoic acid, the mixture thereof, and the mixture of organic carboxylic anhydrides, and carboxylic acid anhydride of carbonic acid, formic acid, and aliphatic ketenes (ketenes, and dimethyl ketene), the mixture thereof and organic carboxylic anhydride, and the like. Among these, acetic anhydride is preferable.

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The amount of the above dehydrating agent is preferably at least 1 time, more preferably 1.2 to 5 times in molar ratio based on 1 mole of the amic acid of the poly(amic acid) varnish. When the amount of the dehydrating agent is less than 1 time in molar ratio based on 1 mole of the amic acid of the poly(amic acid) varnish, there is a tendency that imidization does not proceed sufficiently, resulting in remarkable decrease in mechanical properties of the polyimide film to be obtained. On the other hand, when the amount of the dehydrating agent is more than 5 times, temperature of the belt needs to be raised to evaporate the extra portion of the dehydrating agent, and in consequence, mechanical properties of the polyimide film to be obtained tend to be remarkably decreased. Specifically, tensile strength of the polyimide film to be obtained is lower than 90% of that of the polyimide film prepared by a usual non-fast casting method in which poly(amic acid) varnish is prepared by polymerizing a tetracarboxylic dianhydride component and a diamine component in an almost equimolar ratio, specifically, in a molar ratio of 1:1 to 1:1.005 or 1:1 to 1:0.995.

Among the above chemically-imidizing catalyst, tertiary amines are preferable. Examples of the above tertiary amines are trimethylamine, triethylamine, triethylenediamine, pyridine, picoline, quinoline, isoquinoline, lutidine and the like. Preferable examples are pyridine, β -picoline, γ -picoline, quinoline and isoquinoline. Among these, isoquinoline is preferable.

The amount of the above chemically-imidizing catalyst is preferably at least half time, more preferably 0.6 to 2 times in molar ratio based on 1 mole of the amic acid of the poly(amic acid) varnish. When the amount of the chemically-imidizing catalyst is less than half time in molar ratio based on 1 mole of the amic acid of the poly(amic acid) varnish, mechanical properties of the polyimide film to be obtained is remarkably decreased. Specifically, tensile strength of the polyimide film to be obtained is lower than 90% of that of the polyimide film prepared by a usual non-fast casting method in which poly(amic acid) varnish is prepared by polymerizing a tetracarboxylic dianhydride component and a diamine component in an almost equimolar ratio, specifically, in a molar ratio of 1:1 to 1:1.005 or 1:1 to 1:0.995. The upper limit of the amount of the chemically-imidizing catalyst is preferably 2.0 times. Even if more than 2.0 times of the chemically-imidizing catalyst is added, there is no significant difference in imidizing effect compared to the case where 2.0 times of the chemically-imidizing catalyst is added. Instead, when the amount of the chemically-imidizing catalyst is more than 2.0 times, some portion of the chemically-imidizing catalyst remains in the film and possibly contaminates product line as impurities during steps of preparing print circuit substrates and the like.

The chemically-imidizing agent comprising a dehydrating agent and a chemically-imidizing catalyst may be added to poly(amic acid) varnish directly, but may be dissolved in an organic solvent and then added to poly(amic acid) varnish. Examples of the above organic solvent are N,N-dimethylformamide, N,N-dimethylacetamide, N,N-diethylformamide, N,N-diethylacetamide, N-methylmethoxyacetamide, N-methyl-caprolactam, N-methyl-2-pyrrolidone, tetramethylurea, and the like. These can be used in combination with benzene, benzonitrile, dioxane, xylene, toluene, cyclohexane, and the like. Among these, N,N-dimethylformamide is preferable.

For the purpose of forming a polyimide film stably, fillers such as calcium hydrogen phosphate, silica, mica, titanium oxide, alumina and glass beads may be further added to the above poly(amic acid) varnish.

Subsequently, the above composition of a resin solution obtained by mixing the poly(amic acid) varnish with the chemically-imidizing agent is continuously extruded from a slit die as smooth, thin film curtain and cast on an endless belt. Thereafter, the curtain is dried and heated to form a film of polyimide(amic acid) having self supportability. Then, the film of polyimide(amic acid) is further heat-treated, and a polyimide film having mechanical properties required in the present invention is prepared. At the heat treatment the final heating temperature is preferably 400 to 650° C., more preferably 450 to 600° C., most preferably 480 to 580° C. The heating time is preferably 1 to 600 seconds, preferably 5 to 400 seconds, most preferably 5 to 300 seconds. When the temperature is higher and/or the time is longer than the above, heat deterioration of a film is more likely to occur. When the temperature is lower and/or the time is shorter than the above, characteristics such as mechanical strength tend to decrease.

In the above process, viscosity of composition of a resin solution obtained by mixing the poly(amic acid) varnish with the chemically-imidizing agent in the die is preferably at most 450 poise, more preferably at most 300 poise, most preferably 50 to 300 poise. When the viscosity of the composition of a resin solution is more than 450 poise, unevenness in film thickness increases remarkably, and it is not preferable since bubble inclusion into the resin film occurs easily. On the other hand, when the viscosity of the composition of a resin solution is less than 50 poise, stable film forming becomes difficult in the casting process with a die of the present invention. These viscosity values are measured by a Brookfield type viscometer.

The viscosity of the composition of a resin solution in a die is measured within 2 minutes after mixing the poly(amic acid) varnish with the chemically-imidizing agent.

Temperature of the above composition of a resin solution in a die is preferably at most 20° C., more preferably -10° C. to 10° C. When the temperature of the above composition of a resin solution is more than 20° C. in the die, a resin film is partially imidized, leading to problems with generation of gel defect parts in a film as well as formation of coating streaks since the slit die is clogged with the gel generated by the partial imidization of the poly(amic acid) composition. Also, the case where the temperature of the above composition of a resin solution is less than -10° C. in the die is not preferable since the viscosity of the composition of a resin solution becomes more than 450 poise.

Thickness of polyimide films which can be prepared according to the process of the present invention is not particularly limited. Generally, the thickness of a polyimide film is about 5 to 250 μm, but preferably in the range of about 5 to 100 μm. When the film thickness is less than 5 μm, curtain also becomes thin in thickness to be easily affected by wind and the like, resulting in a tendency that bubbles are easily included. Also, when the film thickness is more than 250 μm, the amount of extrusion increases to make the curtain thick and heavy, and thus there is no problem with bubble inclusion. In this way, it is possible to obtain a polyimide film whose unevenness in thickness in the machine direction is as small as at most 2.0 μm, preferably at most 1.8 μm, more preferably 1.6 μm in R value.

The process for preparing a polyimide film according to the present invention has been explained so far, but the present invention is not limited thereto. The process can be carried out in various embodiments which are improved, modified and changed based on knowledge of persons skilled in the art within the scope of the present invention.

Hereinafter, concrete explanations are made as to the examples, but the present invention is not limited to these

examples. "Part(s)" and "%" in examples mean "part(s) by weight" and "% by weight", respectively, unless otherwise specified.

[Evaluation Method]

1) Measurement of tensile strength

Tensile strength was measured according to ASTM D882.

2) Thickness in machine direction

The center part of the obtained polyimide film was taken out for 5 m in the machine direction as a sample. By using a contact and continuous measuring type thickness meter (film thickness tester KG601A made by Anritsu Corporation), the maximum thickness and minimum thickness was determined from a chart. The thickness in the machine direction was calculated with R as an index of unevenness in thickness by an equation: R value=(maximum thickness)-(minimum thickness). The unit is "μm".

EXAMPLE 1

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether as aromatic diamine were added to DMF in a molar ratio of aromatic tetracarboxylic dianhydride to aromatic diamine of 1:1.02, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 800 poise) was added an imidizing agent comprising 200 g of acetic anhydride, 100 g of isoquinoline and 190 g of DMF, in an amount of 40% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 20 mm below the die. In this case, temperature of the resin solution in the T-die was 0° C. and viscosity of the resin solution was 150 poise at the temperature. Also, the molar ratio of acetic anhydride as the dehydrating agent was 1.67 times, the molar ratio of isoquinoline as the catalyst was 0.66 time based on 1 mole of the amic acid of the poly(amic acid) varnish.

The resin film was dried and imidized at 130° C. for 100 seconds, 300° C. for 20 seconds, 450° C. for 20 seconds and 500° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the film was 1.5 and tensile strength of the film was 255 MPa in the machine direction.

EXAMPLE 2

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride, and 4,4'-diaminodiphenyl ether and paraphenylenediamine in a molar ratio of 3:1 as aromatic diamine were added to DMF in a molar ratio of aromatic tetracarboxylic dianhydride to aromatic diamine of 1:0.98, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 1,000 poise) was added an imidizing agent comprising 200 g of acetic anhydride, 110 g of isoquinoline and 180 g of DMF, in an amount of 40% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 20 mm below the die. In this case, the temperature of the resin solution in the T-die was 0° C. and the viscosity of the resin solution was 180 poise at the temperature.

Also, the molar ratio of acetic anhydride as the dehydrating agent was 1.58 times, the molar ratio of isoquinoline as the catalyst was 0.69 time based on 1 mole of the amic acid

of the poly(amic acid) varnish. The resin film was dried and imidized at 130° C. for 100 seconds, 250° C. for 20 seconds, 400° C. for 20 seconds and 520° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the film was 1.7 and tensile strength of the film was 310 MPa in the machine direction.

EXAMPLE 3

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether as aromatic diamine were added to DMF in a molar ratio of aromatic tetracarboxylic dianhydride to aromatic diamine of 1:1.02, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 800 poise) was added an imidizing agent comprising 180 g of acetic anhydride, 130 g of isoquinoline and 190 g of DMF, in an amount of 50% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 15 mm below the die. In this case, the temperature of the resin solution in the T-die was 0° C. and the viscosity of the resin solution was 100 poise at the temperature.

Also, the molar ratio of acetic anhydride as the dehydrating agent was 1.76 times, the molar ratio of isoquinoline as the catalyst was 1.01 time based on 1 mole of the amic acid of the poly(amic acid) varnish. The resin film was dried and imidized at 140° C. for 100 seconds, 300° C. for 20 seconds, 450° C. for 20 seconds and 500° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the film was 1.7 and tensile strength of the film was 255 MPa in the machine direction.

COMPARATIVE EXAMPLE 1

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether as aromatic diamine were added to DMF in a molar ratio of aromatic tetracarboxylic dianhydride to aromatic diamine of 1:1.02, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 800 poise) was added a chemically-imidizing agent comprising 300 g of acetic anhydride, 40 g of isoquinoline and 150 g of DMF, in an amount of 40% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 20 mm below the die. In this case, the temperature of the resin solution in the T-die was 0° C. and the viscosity of the resin solution was 150 poise at the temperature.

Also, the molar ratio of acetic anhydride as the dehydrating agent was 2.51 times, the molar ratio of isoquinoline as the catalyst was 0.27 time based on 1 mole of the amic acid of the poly(amic acid) varnish. The resin film was dried and imidized at 130° C. for 100 seconds, 300° C. for 20 seconds, 450° C. for 20 seconds and 500° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the film was 1.5 and tensile strength of the film was 185 MPa in the machine direction.

COMPARATIVE EXAMPLE 2

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether and paraphenylenediamine in a molar ratio of 3:1 as aromatic diamine were added to DMF in a molar ratio of aromatic tetracar-

boxylic dianhydride to aromatic diamine of 1:0.98, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 1,000 poise) was added an imidizing agent comprising 300 g of acetic anhydride, 40 g of isoquinoline and 150 g of DMF, in an amount of 40% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 20 mm below the die. In this case, the temperature of the resin solution in the T-die was 0° C. and the viscosity of the resin solution was 200 poise at the temperature. Also, the molar ratio of acetic anhydride as the dehydrating agent was 2.37 times, the molar ratio of isoquinoline as the catalyst was 0.27 time based on 1 mole of the amic acid of the poly(amic acid) varnish. The resin film was dried and imidized at 130° C. for 100 seconds, 250° C. for 20 seconds, 400° C. for 20 seconds and 520° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the film was 1.7 and tensile strength of the film was 210 MPa in the machine direction.

COMPARATIVE EXAMPLE 3

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether as aromatic diamine were added to DMF in a molar ratio of aromatic tetracarboxylic dianhydride to aromatic diamine of 1:1.005, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 4,000 poise) was added DMF of 100% by weight to dilute the mixture, and a poly(amic acid) DMF solution was prepared (concentration of solid content: 10%; viscosity at 20° C.: 1,000 poise). Thereto was added an imidizing agent comprising 300 g of acetic anhydride, 40 g of isoquinoline and 150 g of DMF, in an amount of 20% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 20 mm below the die. In this case, temperature of the resin solution in the T-die was 0° C. and viscosity of the resin solution was 200 poise at the temperature.

Also, the molar ratio of acetic anhydride as the dehydrating agent was 2.5 times, the molar ratio of isoquinoline as the catalyst was 0.26 time based on 1 mole of the amic acid of the poly(amic acid) varnish. In this case, the drying temperature needed to be raised higher in order to dry the composition on the endless belt until self supportability was achieved. Compared to 130° C. in Comparative Example 1, the temperature needed to be 160° C. in this case. The resin film was dried and imidized at 160° C. for 100 seconds, 300° C. for 20 seconds, 450° C. for 20 seconds and 500° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the film was 1.6 and tensile strength of the film was 210 MPa in the machine direction.

COMPARATIVE EXAMPLE 4

Pyromellitic dianhydride as aromatic tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether as aromatic diamine were added to DMF in a molar ratio of aromatic tetracarboxylic dianhydride to aromatic diamine of 1:1.005, and the mixture was polymerized. To the obtained poly(amic acid) DMF solution (concentration of solid content: 20%; viscosity at 20° C.: 4,000 poise) was added an imidizing agent comprising 300 g of acetic anhydride, 40 g of iso-

quinoline and 150 g of DMF, in an amount of 40% by weight based on the poly(amic acid) DMF solution to obtain a composition of a resin solution. Next, the above composition of a resin solution was stirred rapidly by using a mixer, extruded from a T-die and cast on a stainless endless belt running 20 mm below the die. In this case, temperature of the resin solution in the T-die was 0° C. and viscosity of the resin solution was 880 poise at the temperature.

Also, the molar ratio of acetic anhydride as the dehydrating agent was 2.51 times, the molar ratio of isoquinoline as the catalyst was 0.27 time based on 1 mole of the amic acid of the poly(amic acid) varnish. The resin film was dried and imidized at 130° C. for 100 seconds, 300° C. for 20 seconds, 450° C. for 20 seconds and 500° C. for 20 seconds to obtain a polyimide film having an average film thickness of 25 μm. R value of the thickness in the machine direction was turned out to be 3.3 μm when the value was measured by taking out the center part of the film for 5 m in the machine direction as a sample. In examination of the film, numerous bubbles having a diameter of about 5 mm were observed to be included at the both ends of the film. Tensile strength of the film was 255 MPa in the machine direction.

Except for Comparative Example 4, no bubble inclusion was observed at casting, and unevenness in thickness was as small as at most 2.0 μm in R value of the thickness in the machine direction in any of Comparative Examples 1 to 3 and Examples 1 to 3.

As mentioned above, according to the present invention, there can be provided a process for preparing a polyimide film wherein production efficiency can be increased by a stable cast film forming method of high processability. In the process, bubble inclusion is prevented and unevenness in thickness is controlled by adjusting viscosity to low values,

and decrease in mechanical properties, especially tensile strength, of the polyimide film which occurred in die cast processes for preparing a polyimide film with fast casting can be prevented.

What is claimed is:

1. A process for preparing a polyimide film by extruding and casting a composition of a resin solution containing a poly(amic acid) varnish, comprising:

preparing the poly(amic acid) varnish having low viscosity by polymerizing a tetracarboxylic dianhydride component with a diamine component in a molar ratio of 1:1.01 to 1:1.05 or 1:0.95 to 1:0.99, and

preparing the composition of the resin solution by adding to the poly(amic acid) varnish a dehydrating agent in an amount of at least one mole and a chemically-imidizing catalyst in an amount of at least 0.5 mole per 1 mole of amic acid of the poly(amic acid) varnish.

2. The process of claim 1, wherein viscosity of said poly(amic acid) varnish is at most 2,000 poise at 20° C.

3. The process of claim 1, wherein viscosity of said poly(amic acid) varnish is at most 1,500 poise at 20° C.

4. The process of claim 1, wherein viscosity of said poly(amic acid) varnish is 100 to 1,500 poise at 20° C.

5. The process of claim 1, wherein said composition of the resin solution is obtained by adding the dehydrating agent in an amount of 1.2 to 5 moles and the chemically-imidizing catalyst in an amount of 0.6 to 2.0 moles per 1 mole of the amic acid of the poly(amic acid) varnish.

6. The process of claim 1, wherein said chemically-imidizing catalyst is a tertiary amine.

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